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Methods for Field Studies of the Effects of Military Smokes, Obscurants, and Riot-control Agents on Threatened and Endangered Species

Volume 4: Chemical Analytical Methods

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Smokes, obscurants, and riot-control agents constitute a diverse group of chemical compounds that are released into the environment during military training exercises. Concern has been expressed over the use of these compounds and how they may affect threatened and endangered (T&E) species that reside on military installations.

This literature review examines chemical analytical methods (standard and nonstandard) for isolating and detecting the components of smokes, obscurants, and riot-control agents from environmental media (both abiotic and biotic). The report identifies and evaluates possible analytical methods and recommends the methods that are best suited for measuring the analyte of interest. The intent of this report is to provide a basis or starting point for performing analysis on field samples.

The unattached Appendices of this report contain the recommended analytical methods, both standard and nonstandard. The Appendices also include methods for sample collection, transport, storage, and preparation.

Volume 1 of this series will be an overview of the entire study and will include information on applicable regulations. Volume 2 (USACERL Technical Report 97/140, September 1997) reviews methods for assessing ecological risks. Volume 3 will discuss strategies for developing a statistically sound approach to assessing the effects of military smokes, obscurants, and riot-control agents.

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Strategic Environmental Research and Development Program
Improving Mission Readiness through Environmental Research

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Foreword

This study was conducted for the Strategic Environmental Research and Development Program (SERDP) under project number CS-766, "Identification, Assessment, and Mitigation of Impacts of Military Related Chemicals and Pollutants on TES" and project number CS-507, "Threatened, Endangered, and Sensitive Resources: Impact of Smokes and Obscurants on TES." Congress established SERDP through Public Law 101-510 on November 5, 1990 (10 U.S.C. 2901-2904). SERDP is a joint multi-agency (Department of Defense, Department of Energy, and Environmental Protection Agency) effort to support environmental quality research, development, demonstration, and applications programs. The technical monitor at the beginning of this work was Dr. Femi A. Ayorinde, Cleanup and Conservation Program Manager, SERDP.

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The Director of CERL is Dr. Michael J. O'Connor.

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Distribution

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1 Introduction

Background

Historically, smoke was used for signaling on the battlefield. More recently, smoke has been used by the military as screening for combat troops as well as for signaling and tracking (Shinn et al. 1987). The United States was one of the first countries to use white phosphorus to generate smoke and has used other types of smokes and obscurants during the course of two World Wars and other military conflicts (Department of Army 1967, 1974). In spite of long-term historic use by the U.S. military, it was not until the last years of World War I that intense research and development of smoke munitions was conducted by the military. During the period between World War I and World War II, considerable progress was made in the development of smokes, obscurants, and riot-control agents. The latter agent was used by the military for terrain denial and to incapacitate enemy troops and is currently being used in training maneuvers (Keller, Elves, and Bonnin 1986).

Many types and combinations of smokes are used by the military, but the three basic types of screening smokes are (1) fog oil smoke, (2) hexachloroethane (HC) smoke, and (3) white phosphorus (WP) smoke (Kroschwitz and Howe-Grant 1993, Shinn et al. 1987). Fog oil smoke is generated by cooling (via the atmosphere) vaporized oil, thus producing very small oil droplets (0.5 to 1.0 μm). A low viscosity petroleum oil, known as fog oil, is most commonly used in the production of fog oil smoke. The two major components of HC smoke are zinc oxide and hexachloroethane. Upon heating this mixture, zinc chloride-water smoke is produced (Department of Army 1967, Shinn et al. 1987). WP smoke is produced by heating white or red phosphorus. White phosphorus vapor reacts with oxygen in the air to produce dense clouds of phosphorus pentoxide (Department of Army 1967, Shinn et al. 1987). There are other types of smokes and obscurants such as colored smoke (from anthraquinones) used in signaling, and brass and graphite flakes that are used in obscuring infrared signals (Cataldo et al. 1990).

The military's deployment of smoke-generating chemicals over land and water has raised concern for the integrity of that environment. Many military training areas also serve as wildlife habitat for numerous species of animals, including some on the threatened and endangered (T&E) species list. In support of mili-

tary efforts to maintain realistic training while protecting T&E species and their habitat, the U.S. Army Construction Engineering Research Laboratory (CERL) is identifying and developing methods to realistically assess the possible effects of smokes and obscurants used by the military on threatened and endangered species.

Objective

The objective of this phase of research was to conduct a literature search to examine, evaluate, and recommend, as appropriate, any standard analytical methods for isolating and detecting the components of smokes, obscurants, and riot-control agents from environmental media (both abiotic and biotic). In cases where standard methods could not be identified, nonstandard analytical methods were investigated, evaluated, and, when applicable, recommended as possible analytical methods for detecting components of smokes, obscurants, and riot-control agents in abiotic or biotic media.

Approach

Researchers conducted a thorough literature search, including the following databases: BIOSIS, CAS, CA Surveyor, First Search, and Medline. Standard analysis methods for the components of smokes, obscurants, and riot-control agents were examined in the following manuals:

Association of Official Analytical Chemistry (AOAC) *Official Methods of Analysis of AOAC International* (AOAC 1995).

American Public Health Association (APHA) *Standard Methods for the Examination of Water and Wastewater* (APHA 1992).

American Society for Testing and Materials (ASTM) *Annual Book of ASTM Standards – Section 11, Water and Environmental Technology* (ASTM 1993, 1994).

Environmental Protection Agency (EPA) *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020 (EPA 1983).

EPA *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017 (EPA 1988).

EPA *Methods for the Determination of Organic Compounds in Drinking Water*, EPA-600/4-88/039, EPA-600/4-90/020 (Supplement 1), and EPA-600/R-92/129 (Supplement 2) (EPA 1991a).

EPA *Methods for the Determination of Metals in Environmental Samples*, EPA-600/4-91/010 and EPA-600/R-94/111 (Supplement 1) (EPA 1991b).

EPA *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA-600/R-93/100 (EPA 1993).

EPA *Analytical Methods for the Determination of Pollutants in Pharmaceutical Manufacturing Industry Wastewater*, EPA-821-B-94-001 (EPA 1995a).

EPA *Test Methods for Evaluating Solid Waste*, EPA SW-846 (EPA 1995b).

National Institute for Occupational Safety and Health (NIOSH) *NIOSH Manual of Analytical Methods* (NIOSH 1994).

Scientific journals and proceedings from numerous scientific symposiums were consulted for nonstandard analysis methods for the components of smokes, obscurants, and riot-control agents when standard methods were not found in the above list of manuals.

Following is a list of the investigated smokes, obscurants, and riot-control agents. Each chemical is discussed in detail in the following chapters.

Chemicals used to produce smokes and obscurants:

Anthraquinone (colored smokes), Chapter 2

Brass, Chapter 3

Fog Oil, Chapter 4

Graphite, Chapter 5

Hexachloroethane, Chapter 6

Terephthalic Acid, Chapter 7

Titanium Dioxide, Chapter 8

Red Phosphorus, Chapter 9

White Phosphorus, Chapter 10

Polyethylene Glycol, Chapter 11

Chemicals used as riot-control agents:

(o-Chlorobenzal)malononitrile, Chapter 12

Dibenz(b,f)-1,4-oxazepine, Chapter 13

Report Organization

Each chapter identifies possible analytical methods, discusses development trends, and evaluates and recommends selected methods. To provide an easy assessment of the time and cost for the analysis, an overview of the chemicals, equipment, and procedures for the recommended methods also is included.

Copies of the recommended methods are provided in the unattached appendices of the report. Appendices A and B list the standard and nonstandard methods, respectively. Analytical methods, organized by chemical compound, are presented in Appendices C through M. Sample collection, transport, and storage methods are listed in Appendix N, while methods of sample preparation are listed in Appendix O. Since some of the analytical methods contain instructions about sample collection, transport, storage, and preparation as part of the analysis procedure, the reader is advised to review the analytical method completely and consult Appendix N and/or Appendix O when applicable.

The Unattached Appendices are not posted to the World Wide Web. The 766-page volume is available from the National Technical Information Service, 5385 Port Royal Road, Springfield, VA 22161.

Scope

This report provides a basis or starting point for performing analysis on field samples. The recommended methods, in most cases, reflect the current state of technology in analytical chemistry at the time the report was prepared. Because methods may have been revised or updated, you are advised to verify that you are using the most current version. Standard methods were identified first, as these are techniques that have matured to a level of routine analysis. Most methods listed in each chapter in the section titled “Possible Methods” can be used without modification or change. Methods mentioned in each chapter in the section titled “Development Trends” generally reflect the latest technique(s) in assaying for the analyte of interest. However, the majority of these methods need further development. Thus, these methods are noted to serve as a guide for those media not yet thoroughly researched or where techniques or methods have

not been developed completely. Finally, the methods discussed in each chapter in the section titled “Recommended Methods” are, at the time of this literature search, those best suited for measuring the analyte of interest.

The methodologies discussed in this report are recommended for analyses of field samples for residues of smokes, obscurants, and riot-control agents. Results of such analyses will assist assessment of potential impacts of smokes, obscurants, and riot-control agents on threatened and endangered (T&E) species at military installations.

Mode of Technology Transfer

This research will be distributed to selected military organizations that are particularly concerned with smokes, obscurants and riot-control agents. The report will also be posted to the World Wide Web, making it accessible to installations where smokes and obscurants (or riot-control agents) are used and where endangered, threatened, or candidate species are known to occur or may be present.

2 Anthraquinone

Use and Properties

Anthraquinones, which are produced naturally and synthetically, belong to a group of functionally diverse chemical compounds that are used in the manufacturing of products such as colorants in food, drugs, cosmetics, hair dyes, and textiles (Sendelbach 1989). Anthraquinones and analogs of anthraquinones, including 1-methylaminoanthraquinone, 1-aminoanthraquinone, 1,8-di-p-toluidinoanthraquinone, and 1,4-diaminoanthraquinone, are used by the military to generate colored smoke (Department of Army 1974). These organic dyes produce colors such as red, yellow, green, and violet, depending on which subunit (i.e., amino, hydroxyl, alkyl, aryl, chloro, or bromo) is attached to the ring structure. The color quality of the smoke generated by anthraquinones is better than other color smoke-producing agents (Department of Army 1967). Table 2-1 lists some common properties of anthraquinone.

Table 2-1. Chemical and physical properties of anthraquinone.

Chemical Name	Anthraquinone
Synonyms	9, 10-Anthracenedione 9, 10-Anthraquinone Anthracene-9,10-quinone Anthradione Hoelite Morkit
CAS (Chemical Abstracts Service) Registry Number	84-65-1
Molecular Formula	$C_{14}H_8O_2$
Molecular Weight	208.20
Physical Description	Colorless, Orthorhombic, Bipyramidal Crystals
Density	
Melting Point	

Possible Methods

Standard Methods

There is no specific standard analytical method for anthraquinone. However, there are methods for polycyclic aromatic hydrocarbons (PAH), semivolatile organic compounds, and analogs of anthraquinone.

In *Annual Book of ASTM Standards,* Vol. 11.02 (ASTM 1994):
Method D5412-93 — for PAH mixtures in water using fluorescence spectroscopy.

In *Annual Book of ASTM Standards,* Vol. 11.02 (ASTM 1993):
Method D4657-92 — for PAHs in water; uses high-performance liquid chromatography (HPLC).

In *Standard Methods for the Examination of Water and Wastewater* (APHA 1992):
Methods 6440B and C — for PAH monitoring in water and wastewater by using HPLC, gas chromatography/mass spectroscopy (GC/MS), and gas chromatography (GC).

In *Test Methods for Evaluating Solid Waste,* EPA SW-846 (EPA 1995b):
Method 4035 — this method uses an immunoassay to screen for PAH in soil when the concentration is above 1 mg/kg. The commercially available PAH kit is sensitive to PAH compounds comprised of three to four member rings. (This method was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).
Method 8100 — GC method measuring certain PAHs using both packed and capillary columns.
Method 8270C — for quantifying semivolatile organic compounds, including 2-aminoanthraquinone, in waste, soil, and groundwater using GC/MS with capillary column. (This method has been revised and was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).
Method 8310 — HPLC method for determining PAH from soil, groundwater, and waste.
Method 8321A — this method uses HPLC methods coupled with thermospray/mass spectrometry or with ultraviolet (UV) detection to determine nonvolatile compounds in soil, water, and waste matrices. Analogs of anthraquinone are listed as some of the analytes that can be detected with this method. (This method has been revised and was announced for public com-

ments in the Federal Register on July 25; the comment period ended on September 25, 1995).

Method 8410 — for identifying extractable semivolatile organic compounds in wastewater, soils and sediments, and solid wastes using gas chromatography/Fourier transform infrared (GC/FT-IR) spectrometry.

Method 8275A — used in qualitatively screening semivolatile organic compounds from nonaqueous solid wastes and soils using thermal chromatography/mass spectrometry (TC/MS). (This method has been revised and was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).

In *Methods for the Determination of Organic Compounds in Drinking Water*, EPA-600/4-88/039, EPA-600/4/90/020 (Supplement 1), and EPA-600/R-92/129 (Supplement 2) (EPA 1991a):

Method 550 — PAH determination in drinking water by liquid-liquid extraction and HPLC coupled to UV and fluorescence detectors.

Method 550.1 — PAH determination in drinking water by liquid-solid extraction and HPLC coupled to UV and fluorescence detectors.

In *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017 (EPA 1988):

Method TO13 — PAH determination in ambient air by GC and HPLC methods.

In *NIOSH Manual of Analytical Methods* (NIOSH 1994):

Methods 5506 and 5515 — for PAH monitoring in air using HPLC and GC, respectively.

In *Official Methods of Analysis of AOAC International* (AOAC 1995):

Method 973.30 — PAH determination in food products employing UV spectrophotometry.

Nonstandard Methods

The following methods are nonstandard analytical methods that specifically test for anthraquinone and/or analogs of anthraquinone.

"Gas chromatographic screening of organic compounds in urban aerosols" (Aceves and Grimalt 1992):

This paper describes methods for detecting organic compounds including anthraquinone in urban aerosols. The authors describe analytical techniques involving GC/MS procedures with different capillary columns.

"Photolysis of smoke dyes on soils" (Adams, Weber, and Baughman 1994):

This paper is mainly about photolytic effects of smoke dyes on soil surfaces. Soil samples are spiked with anthraquinone and azo dyes and incubated at conditions that mimic field conditions. The authors provide a brief summary of their analytical methods in detecting smoke dyes (including analogs of anthraquinone) and its degradation products in soil. The method includes solvent extraction followed by HPLC and GC analyses.

"Identification of oxygen derivatives of polycyclic aromatic hydrocarbons in airborne particulate matter of upper Silesia (Poland)" (Bodzek, Tyrpien, and Warzecha 1993):

This paper describes a method for identifying PAHs, including anthraquinone, in airborne particulate matter. The authors use GC/MS as well as thin layer chromatography (TLC) techniques to identify the analytes being monitored.

"Separation and determination of reaction mixtures of anthraquinone by gas chromatography" (Husain et al. 1994):

This paper describes a GC method for determining anthraquinone and its analogs. This method aids in separating and identifying various mixtures of anthraquinone but does not provide any environmental sampling procedures.

"Isolation and determination of alizarin in cell cultures of *Rubia tinctorum* and emodin in *Dermocybe sanguinea* using solid-phase extraction and high performance liquid chromatography" (Toth et al. 1993):

This paper describes a method for identifying naturally occurring anthraquinones, alizarin and emodin, from plant extracts of *R. tinctorum* and mushroom extracts of *D. sanguinea*. Alizarin and emodin are extracted from plant and mushroom cells with 80% ethanol. The extracts are then purified by solid-phase extraction (SPE) procedures using the C_8 cartridges and identified by HPLC with UV detection. The analyte recovery is estimated to be 95 to 99% efficient when SPE procedures are used. This method may be useful in detecting and/or isolating naturally or synthetically produced anthraquinones or analogs of anthraquinone from vegetation samples.

Development Trends

Abiotic Media

Most of the standard and nonstandard methods listed earlier describe various sample collection techniques, depending on the sampling matrix; but sample

preparation steps are similar whether the sample matrix is air, water, or solid waste. Upon collection, samples are extracted with an organic solvent and usually undergo a cleaning process before analyses. In most cases, analytes are identified either by an HPLC with fluorescence or a UV detector, a GC/MS with a flame ionization detector (FID) or photoionization detector (PID), or capillary column-GC with an FID.

Biotic Media

Many nonstandard analytical methods are used to extract and analyze naturally occurring anthraquinones and analogs of anthraquinone from bacteria and plant samples. The separation and detection techniques for most of these methods are similar to methods listed in the previous section (*Abiotic Media*) (Demirezer and Rauwald 1994; Itoh, Yatome, and Ogawa 1993; Nishimura and Mizutani 1995; Toth et al. 1993). Analytical methods for sampling biological fluids such as blood and urine have not been identified. Toxicological studies involving anthraquinones usually involve exposure to the compound and assaying of biochemical parameters in blood, urine, liver, and/or kidney rather than assaying for the compound itself (Sendelbach 1989).

Recommended Methods

Standard Methods

EPA Method 8270C and EPA Method 8321A from *Test Methods for Evaluating Solid Waste* (EPA 1995b) are the only two methods that specifically assay for analogs of anthraquinone along with PAH and other semivolatile compounds. EPA Method 8321A uses the more sensitive technique of HPLC with thermal chromatography/mass spectrometry (TC/MS) or UV detection; EPA Method 8270C uses GC/MS to detect anthraquinone compounds. However, EPA Method 8270C provides more detailed sample preparation and analysis steps for anthraquinone analogs compared to EPA Method 8321A. Therefore, EPA Method 8270C is recommended for determining anthraquinone compounds in solid waste and groundwater. This method can also be used to analyze soil and water samples. EPA Method 8270C is a versatile method in that it can be used to test a variety of matrices.

NIOSH Method 5506 from the 1994 *NIOSH Manual of Analytical Methods* (NIOSH 1994) is recommended for determining anthraquinone compounds from air samples. Although this method does not specifically assay for anthraquinones, the separation and detection steps outlined can be used to assay for

anthraquinone compounds by determining their retention times. NIOSH Method 5506 is more sensitive than NIOSH Method 5515 and less complicated and time consuming than EPA Method TO13. Table 2-2 lists a brief summary of the recommended standard methods for anthraquinone.

Table 2-2. Recommended standard methods for anthraquinone analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Solid waste	collect samples in glass container and store at 4°C	extract with organic solvents	GC	MS	not provided	$450
Groundwater	collect samples in glass container and store at 4°C	extract with organic solvents	GC	MS	20 µg/L	$420
Air	store filter and sorbent tubes in culture tubes at 0°C and shield from light	extract with organic solvents	HPLC	Fluorescence/ UV	1 to 50 $\mu g/m^3$ for 400 L of air	$300

* See Appendix A for a list of the standard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Nonstandard Methods

The nonstandard methods listed previously specifically analyze for anthraquinone or analogs of anthraquinone, or include anthraquinone as one of the analytes being monitored. However, only a few of the papers reviewed provide descriptive procedures for sample preparations that are applicable to field situations. The method described by Adams, Weber, and Baughman (1994) is very brief regarding sample preparation, and the limit of detection for the assay is not provided. Both Aceves and Grimalt (1992) and Bodzek, Tyrpien, and Warzecha (1993) describe methods for detecting organic compounds, including anthraquinones, in air samples. However, their methods are not much better than the standard methods for detecting PAHs and semivolatile compounds. Husain et al. (1994) provides a rapid and selective GC method for detecting anthraquinone and its analogs, but fails to provide any sample preparation steps. Finally, Toth et al. (1993) provides a method for extracting and identifying naturally occurring anthraquinones from plant and mushroom cells. This method can be modified to detect anthraquinones originating from smoke dyes rather than naturally occurring anthraquinones in plant cells. Therefore, this method can be used as a field screening method for detecting anthraquinone contamination in

vegetation. Table 2-3 lists a brief summary of the recommended nonstandard method for anthraquinone.

Table 2-3. Recommended nonstandard method for anthraquinone analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Plant/ vegetation	samples are frozen or dried	ethanol and SPE	HPLC	UV	0.156 µg/ml	$350

* See Appendix B for a list of the nonstandard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Procedures

Groundwater and Solid Waste Samples — EPA Method 8270C

Sample Collection, Transport, and Storage QA/QC

Collect all samples in a wide-mouthed glass container with a teflon-lined lid. Store samples at 4°C. Extract samples within 14 days of collection and analyze the extracts within 40 days of extraction. These guidelines are provided in unattached Appendix N of this report (Chapter Four - Organic Analytes, Section 4.1 - Sampling Considerations, from EPA SW-846 [EPA 1995b]).

Sample Preparation

The recommended sample preparation techniques for 2-aminoanthraquinone are EPA Method 3510C for water samples and EPA Method 3580A for solid waste samples.

EPA Method 3500B — Organic Extraction and Sample Preparation

This method provides guidelines and recommendations on organic extractions and sample preparation procedures.

EPA Method 3510C — Separatory Funnel Liquid-Liquid Extraction

This method involves extracting organic compounds from a water sample of 1 liter with 60 ml of methylene chloride at pH >11. Repeat the process three times; collect and combine the extracts. Concentrate the extract using the Kuderna-Danish (K-D) apparatus until reaching a final volume of 1 ml.

EPA Method 3580A — Waste Dilution

This method involves a solvent dilution of nonaqueous waste samples. Place a sample weight of 1 gram in a 10-ml volumetric flask. Add 10 ml of methyl-

ene chloride, followed by 2 grams of anhydrous sodium sulfate. Shake the mixture for approximately 2 minutes and filter it through Pasteur pipettes plugged with 2 to 3 cm of glass wool. The extract is ready for analysis or cleanup.

If needed, extracts may be cleaned before GC/MS analysis as described in EPA Methods 3611B, 3630C, or 3640A.

EPA Method 3611B — Alumina Column Cleanup and Separation of Petroleum Wastes

Clean the extracts by eluting the sample through a column packed with alumina and anhydrous sodium sulfate. Load 1 ml of sample and 1 ml of hexane onto the column and elute with 100 ml of methylene chloride.

EPA Method 3630C — Silica Gel Cleanup

This method offers two options to clean sample extracts: solid-phase extraction cartridges or standard chromatography column techniques. However, for PAH-type compounds, the standard chromatography column technique is recommended. Generally, the standard chromatography column technique offers greater cleanup capabilities due to the greater amount of silica gel packing. Pack the column with a slurry of activated silica gel that has been mixed with methylene chloride. Add anhydrous sodium sulfate on top of the silica gel layer and pre-elute the column with pentane. Load the sample extract in cyclohexane (2 ml) and an additional 2 ml of cyclohexane solvent onto the column and elute with 25 ml of pentane. Discard the pentane eluate.

EPA Method 3640A — Gel Permeation Cleanup

This method is recommended for eliminating lipids, polymers, copolymers, proteins, and natural resins from sample extracts. This method involves size exclusion cleanup with organic solvents and hydrophobic gels. Pack a gel permeation cleanup column with Bio Beads and flush with methylene chloride. After calibrating the column, load the sample extracts in methylene chloride.

Separation and Detection Parameters

1. Set the GC/MS system with the following operating conditions:

Parameter	Setting
Mass range	35-500 amu
Scan time	1 sec/scan
Initial temperature	40°C, hold for 4 min
Temperature program	40-270°C at 10°C/min
Final temperature	270°C, hold until benzo[g,h,i] perylene has eluted
Injector temperature	250-300°C
Transfer line temperature	250-300°C
Source temperature	According to manufacturer's specifications
Injector	Grob-type, splitless
Sample volume	1-2 µl
Carrier gas	Hydrogen at 50 cm/sec or Helium at 30 cm/sec

2. Calibrate the GC/MS with:
   - the tuning standard decafluorotriphenylphosphine (DFTPP, 50 ng = 1 µl)
   - internal standards
   - calibration standards
3. Calibrate GC/MS every 12 hrs with:
   - DFTPP
   - system performance check compounds (SPCC)
   - calibration check compounds (CCC)
   - calibration standards
4. Screen samples through GC/FID or GC/PID before GC/MS analysis to minimize contamination with high levels of organic compounds.
5. Inject 1 µl of the sample into the GC/MS. (If the response exceeds the range of the calibration curve, dilute the sample.)
6. Identify the analyte by comparing the sample and standard mass spectra. (The retention time for 2-aminoanthraquinone under these conditions is 30.63 min. The primary ion is 223 and the secondary ions are 223, 167, and 195.)
7. Calculate the concentration of the analyte(s) and report results in µg/L for water samples and µg/kg for solid samples.

Equipment and Chemical List

1. Equipment:
   a. Gas chromatograph/mass spectrometer system
      - gas chromatograph equipped with:
        • temperature programming
        • splitless injection
        • silicone-coated fused silica capillary column (DB-5, 30 m x 0.25 or 0.32 mm ID, 1 µm film thickness)

- FID or PID detector
- all accessory materials such as gases and syringes

- mass spectrometer capable of:
  - scanning from 35 to 500 amu every 1 sec or less
  - using 70 electron-Volts (eV) in the electron impact ionization mode
  - producing a mass spectrum of the tuning standard [1 µl of DFTPP (50 ng)]
  - interfacing with the GC to produce acceptable calibration points at 50 ng of each compound in interest
- data logging system that is capable of:
  - interfacing with the GC/MS
  - storing continuous data and capable of plotting files in Extracted Ion Current Profile (EICP)

b. Analytical balance with the capacity to weigh 0.1 mg
c. Bottles: amber colored glass with teflon-lined screw caps or crimp tops
d. Volumetric flasks, class A, with ground glass stoppers
e. Extractor (Soxhlet, Sonicator)
f. Kuderna-Danish apparatus
g. Assorted glassware (i.e., pipettes, vials, volumetric flasks, syringes, separatory funnels)
h. Microsyringes.

2. Reagents:
   a. Reagent grade chemicals must be used for all tests. This includes all chemicals (and water) used in stock or standard solutions: acetone, hexane, methylene chloride, isooctane, carbon disulfide, and toluene
   b. Standard Solutions: Suggested internal standards: 1,4-dichlorobenzene-d_4; naphthalene-d_8; acenaphthene-d_{10}; phenanthrene-d_{10}; chrysene-d_{12}; perylene-d_{12}
   c. GC/MS tuning standard: DFTPP plus 4,4-DDT and pentachlorophenol and benzidine
   d. Calibration standards: five calibration standards with concentrations ranging from just above the limit of detection and not exceeding the working range of the GC/MS system
   e. System performance check compounds: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitro-phenol; 4-nitrophenol
   f. Calibration check compounds: acenaphthene; 1,4-dichlorobenzene; hexachlorobutadiene; n-nitrosodiphenylamine; fluoranthene; benzo(a)-pyrene
   g. Surrogate standards - prepare as described in Method 3500B.

Air Samples — NIOSH Method 5506

Sample Collection, Transport, and Storage QA/QC

1. Collect 200 to 1000L of air at a rate of 2 L/min with a calibrated sampling pump equipped with a PTFE (polytetrafluroethylene)-laminated membrane filter and a sorbent tube. Guidelines for air sample collection are provided in unattached Appendix N of this report (Section D - General Considerations for Sampling Airborne Contaminants, from the *NIOSH Manual of Analytical Methods* [NIOSH 1994]).
2. Take additional air samples in the same area to be used for solvent determination.
3. Transfer filter to culture tubes immediately after sampling. Cap culture tubes and sorbent tubes and wrap both sets of tubes with aluminum foil. Store samples in refrigerator (0°C) until use. Label the culture and sorbent tubes with pertinent information including time of collection, temperature, humidity, and atmospheric pressure.

Sample Preparation

1. Extract the analyte from filters with 5 ml of the selected solvent (acetonitrile, benzene, cyclohexane, or methylene chloride) and let it stand in an ultrasonic bath for 15 to 20 min. (Choose the solvent that yields the highest recovery.)
2. Desorb the analyte from the sorbent tubes with 5 ml of acetonitrile and let it stand for 30 min with occasional stirring. Filter the samples through a 0.45-µm syringe filter.
3. Determine the desorption and recovery efficiencies for every lot of filters and sorbent tubes. Spike filters and tubes with five levels of standard solution and incubate overnight. Check the desorption and recovery efficiencies by extracting with solvents used in test samples.

Separation and Detection Parameters

1. Calibrate the HPLC with at least six standard working solutions ranging in concentration from 0.002 to 2.5 µg/ml. Also analyze blank media and reagent samples.
2. Make daily calibrations with at least six standard working solutions and generate a calibration curve. Take standard measurements interspersed between sample measurements.
3. Inject 10 to 50 ml of sample extract into the HPLC with the following conditions: UV @254 nm, fluorescence @340 nm and 425 nm, column equilibrated with 60% CH_3CN/40% H_2O at 1 ml/min at ambient temperature.
4. Measure peaks and determine the concentration of the analyte in air (mg/m^3).

Equipment and Chemical List

1. Equipment:
   a. Personal sampling pump equipped with a PTFE-laminated membrane filter connected to sorbent tube
   b. HPLC equipped with a fluorescence/UV detector and a reverse-phase column (15 cm x 4.6 mm, 5 µm C18)
   c. Electronic integrator
   d. Kuderna-Danish extractor
   e. Ultrasonic bath
   f. Vials, volumetric flasks, culture tubes, syringes, pipettes, fluorescent lighting, aluminum foil.
2. Reagents:
   a. Pesticide grade benzene, cyclohexane, and methylene chloride
   b. Acetonitrile (HPLC grade), degassed
   c. Water, distilled, deionized, degassed
   d. PAH reference standards
   e. Calibration stocks.

Plant/Vegetation Samples — Toth et al. (1993)

This is a nonstandard method that describes the isolation and identification of alizarin and emodin, analogs of anthraquinone, in plant and mushroom extracts using HPLC techniques (Toth et al. 1993). To assay for anthraquinone, modifications may be needed in the extraction procedure. Anthraquinone eludes in approximately 4 min under the HPLC conditions described in this method.

Sample Collection, Transport, and Storage QA/QC

Collect plant and mushroom samples and freeze within 8 hrs of collection. Store at -20°C or dry and pulverize into powder.

Sample Preparation

1. Prepare crude extracts from plant and mushroom samples in the following manner:

   For plants: Extract approximately 10 mg of sample with 2.5 ml of 80% ethanol by sonicating for 5 min and incubating the mixture for 0 to 10 hr at 80°C. Centrifuge the sample and decant and save the supernatant in another test tube. Resuspend the residue with 1.5 ml of 80% ethanol and incubate for another 4 hr at 80°C. Centrifuge the sample again and combine the supernatant with the previous one. Evaporate the combined supernatants to dryness and reconstitute with 1 ml of 80% ethanol.

   For mushrooms: Extract approximately 100 g of the sample with 100 ml of 94% ethanol for 48 hr at room temperature. Filter the sample and concen-

trate it with a rotary evaporator. Acidify the sample (approximately 60 ml) with 1N HCl and further extracte with ether. Evaporate the ether phase and fractionate the sample by flash chromatography using a 1.6 x 22-cm glass column containing silica phase. Elute different fractions by changing the concentration of dichloromethane:methanol:acetic acid gradient. (Emodin was found mostly in the first fraction with 95:5:0.5 CH_2Cl_2:MeOH:HAc gradient.) Evaporate the fraction. Dissolve the residue as well as the precipitate that was formed during the acidification process, in dimethyl sulfoxide (DMSO). The sample preparation procedure for emodin in mushrooms is found in the method by von Wright et al. (1992).

2. Dilute 1 ml of crude extract with water (ten-fold) and pass through a preactivated C_8 SPE cartridge one drop at a time. Wash the cartridge with 2 ml of water followed by 1 ml of methanol:water (30:70). Air dry the cartridge and elute the analytes with 1 ml of methanol:water (80:20, v:v).

Separation and Detection Parameters

1. Inject the sample through a loop injector connected to the HPLC system (see equipment list for setting conditions).
2. Isocratically elute the samples and identify the peaks of the analytes by their retention time, ratiogram plots, and UV-spectra. Compare these results to those of the standards to make positive confirmation of the identity of the analyte. Report the concentration in mg of analyte per gram of sample.
3. Generate standard curves for anthraquinone, alizarin, and emodin. Anthraquinone concentrations ranging from 156 to 20000 ng/ml are found to be linear. The recovery efficiencies of the extraction process are approximately 95% and 99% for emodin and alizarin, respectively. The authors do not specifically state the procedure for determining the recovery efficiencies, but do state that the precision of the assay is approximately 1.5% for n=6.

Equipment and Chemical List

1. Equipment:
   a. An HPLC system equipped with and conditions set at the following:
      - solvent delivery module and controller
      - variable wavelength detector (254 and 280 nm)
      - 20 µl injector loop
      - two-chamber ratiogram recorder
      - chromatogram quantitation signaler with integrator
      - ODS Hypersil reversed-phase column (5 µm particle size, 125 mm x 4.0 mm ID)
      - mobile phase with methanol:5% acetic acid (pH 3.0) (70:30) with a flow rate of 1.0 ml/min

b. SPE cartridges (Bond Elut LRC C_8, 1 ml)
c. Sonicator
d. Centrifuge
e. Rotatory evaporator
f. Test tubes, glass vials, flasks, and beakers
g. Glass column containing silica phase (1.6 x 22 cm).

2. Reagents:
   a. Methanol (HPLC grade)
   b. Ethanol
   c. Water (purified by Millipore system)
   d. Acetic acid (analytical reagent-grade)
   e. Standard solutions:
      - anthraquinone (15-20000 ng/ml)
      - alizarin (78-10000 ng/ml)
      - emodin (312-10000 ng/ml)
   f. Ether
   g. Dichloromethane (CH_2Cl_2)
   h. Dimethyl sulfoxide (DMSO).

3 Brass

Use and Properties

Brass in flake or powder form is one of the components of screening smoke grenade M76 (Palmer 1992, Cataldo et al. 1990, Wentsel and Guelta 1986). Smoke munitions containing metal flakes or powders are used by the military to screen against range finders, thermal surveillance systems, and laser target designators as well as to provide protection for armored vehicles (Hancox and Nicholls 1990, Hancox 1989, Briere et al. 1992). Smoke screens containing brass performed the best against far infrared bands but did poorly on visible light bands (Palmer 1992). Brass is a metal alloy comprised mostly of copper (70%) and zinc (30%) with approximately 1% contamination of trace metals (Cataldo et al. 1990, Wentsel and Guelta 1986, Hancox and Nicholls 1990). Table 3-1 lists some common properties of brass.

Table 3-1. Chemical and physical properties of brass.

Chemical Name	Brass
Synonyms	ß-Brass Rich Gold 7000 Rich Gold 4L7
CAS Registry Number	12597-71-6
Molecular Formula	
Molecular Weight	
Physical Description	yellow-white powder
Density	1.2 g/cm^3
Melting Point	

Possible Methods

Standard Methods

As mentioned above, brass is a metal alloy comprised primarily of copper and zinc. The methods listed in this section are standard analytical methods for cop-

per and zinc, or metals that included copper and zinc as some of the analytes being detected.

In *Annual Book of ASTM Standards*, Vol. 11.01 (ASTM 1994):

Method D1688-90 — for copper in water and Method D1691-90 — for zinc in water using atomic absorption spectrophotometry (AAS).

Methods D4190-82, D4691-87, D3919-85, and D1976-91 —methods for elements/trace metals including cooper and zinc in water using direct current plasma argon emission spectroscopy (DCP-AES), flame atomic absorption spectrophotometry (FLAAS), graphite furnace atomic absorption spectrophotometry (GFAAS), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

In *Standard Methods for the Examination of Water and Wastewater* (APHA 1992):

Methods 3111B and C — for copper and zinc in water using FLAAS method. This method is the same as EPA method 220.1 for copper and 289.1 for zinc.

Method 3113B — for copper in water using the GFAAS technique. This method is the same as EPA method 220.2.

Method 3120 — for copper and zinc in water using ICP-AES. This method is the same as EPA method 200.7 for copper and zinc.

Method 3500D — for copper in water using the neocuproine method.

Method 3500E — for copper in water using the bathocurporine method (used for potable waters).

Methods 3500D and E — for zinc in water using dithizone method I and II, respectively. These methods are colorimetric tests used for potable and polluted waters.

Method 3500F — for zinc in water using zincon method (used for polluted and potable waters).

In *Test Methods for Evaluating Solid Waste*, EPA SW-846 (EPA 1995b):

Methods 6010A and 6020 — for detecting metals, including copper and zinc, in water, soil, and waste mediums using ICP-AES (for copper) and inductively coupled plasma-mass spectrometry (ICP-MS, for zinc).

Methods 7210 and 7211 — for copper and Methods 7950 and 7951 — for zinc in water, soil, and waste material using the FLAAS and GFAAS, respectively.

In *Methods for the Determination of Metals in Environmental Samples*, EPA-600/4-91/010 and EPA-600/R-94/111 (Supplement 1) (EPA 1991b):

Method 200.7 — for detecting metals, including copper and zinc in water and wastewater using ICP-AES.

Method 200.8 — for detecting trace metals, including copper and zinc in water and wastewater using ICP-AES.

Method 200.9 — for detecting metals, including copper in water, waste, and wastewater using a stabilized temperature GFAAS.

Method 200.10 — for detecting metals, including copper in marine waters using ICP-MS.

Method 200.11 — for detecting metals, including copper and zinc in fish tissues using ICP-AES.

Method 200.15 — for detecting metals, including copper and zinc in water by ultrasonic nebulization ICP-AES.

In *Methods for Chemical Analysis of Water and Wastes,* EPA-600/4-79-020 (EPA 1983):

The majority of the metal methods in this manual are becoming obsolete due to the similarity of methods in the APHA manual.

Methods 220.1 and 220.2 — for detecting copper in water and waste samples using FLAAS and GFAAS, respectively.

Methods 289.1 and 289.2 — for detecting zinc in water and waste samples using FLAAS and GFAAS methods, respectively.

In *NIOSH Manual of Analytical Methods* (NIOSH 1994):

Method 7300 — for copper and zinc detection in air using ICP-AES, and Method 7029 — for copper as fume/dust in air using FLAAS.

Methods 8005 and 8310 — monitor elements/metals in blood and urine, respectively. These two methods use ICP-AES.

In *Official Methods of Analysis of AOAC International* (AOAC 1995):

The methods listed in this section pertain to environmental matrices or biological fluids.

Methods 983.24 and 991.11 — use the AAS methods to determine copper and zinc, respectively, in serum.

Method 974.27 — uses the AAS methods to determine copper and zinc in water samples.

Method 990.8 — uses ICP-AES to determine metals, including zinc and copper, in solid waste.

Method 993.14 — uses ICP-MS to determine trace elements, including zinc and copper, in water and wastewater.

Methods 953.01, 975.03, 980.03, and 985.01 — analysis of metals including copper and zinc in plants by using atomic emission spectroscopy (AES), AAS, direct reading spectrograph, and ICP-AES, respectively.

Development Trends

Abiotic Media

The assessment of brass is done by detecting the two major components of brass: copper and zinc. Analytical methods for copper and zinc in abiotic mediums are well established; the majority of these methods involve using ICP-AES, ICP-MS, FLAAS, and GFAAS techniques (ASTM 1994 and 1993, APHA 1992, EPA 1995b, 1991b, and 1983, NIOSH 1994, AOAC 1995, Cataldo et al. 1990, Wentsel and Guelta 1986). Most of these methods are listed above. Some new developments in detecting transitional metals, including copper and zinc in water samples, involve ion chromatographic separation with UV detection, reverse-phase HPLC, and TLC (Nair, Saari-Nordhaus, and Anderson 1994; Medanic, Ivankovic, and Turina 1993; and Li et al. 1993). However, the advantages of these new methods over the older methods are not well described.

Biotic Media

Analytical methods for sampling of biotic mediums such as fish tissues, blood, urine, and vegetation use similar detection methods as described in the "Abiotic Media" section. Examples of these methods are listed in the "Possible Methods" section.

Recommended Methods

Table 3-2 lists a brief summary of the recommended standard methods for brass analysis. EPA Methods 6010A, 6020, 7210, 7211, 7950, and 7951 from EPA SW-486 (EPA 1995b) are capable of detecting copper and zinc from water, soil, and waste mediums. These methods are more versatile in that the same method can be used to test or sample more than one type of environmental matrix. However, EPA Methods 7211 and 7951 use the GFAAS technique, which is more sensitive than the ICP-AES technique used in EPA Method 6010A, and the FLAAS technique used in EPA Methods 7210 and 7950. EPA Method 6020 uses the ICP-MS technique, which generally has a lower limit of detection compared to GFAAS but the method itself does not provide adequate limit of detection information for various environmental matrices. EPA Methods 7211 and 7951 are recommended for detecting copper and zinc in the soil, water, and waste mediums.

NIOSH Methods 7300 and 7029 from the *NIOSH Manual of Analytical Methods* (NIOSH 1994) are the only two methods that sample the air matrix for elements including copper and zinc, and copper dust. Although NIOSH Method 7029 may

provide a more sensitive method for detecting copper, NIOSH Method 7300 is more practical in application since it can be used to measure both copper and zinc. NIOSH Method 7300 is recommended for detecting copper and zinc from air samples.

Table 3-2. Recommended standard methods for brass analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Water	collect samples in a clean glass or plastic bottle and acidify with HNO_3 to pH < 2 and store at 4°C	microwave assisted acid digest	AAS	GF	1 µg/L for Cu 0.05 µg/L for Zn	$25
Soil and waste	collect samples in a clean glass or plastic bottle and acidify with HNO_3 to pH < 2 and store at 4°C	microwave assisted acid digest	AAS	GF	1 µg/L for Cu 0.05 µg/L for Zn	$30
Air	remove filter holder and cap tightly; place in a suitable container and ship to the lab as soon as possible	acid digest	AES	ICP	2 ng/ml for Cu 0.6 ng/ml for Zn	$40
Urine	collect 50 ml of urine and preserve with 5 ml of HNO_3 in a PE bottle; ship in refrigeration	extract analytes with resin; acid digest	AES	ICP	0.1 µg per sample for Cu and Zn	$130
Blood and tissue	collect blood in a heparinized tube and freeze until use collect and freeze 0.25 to 1 g of tissue until use	acid digest	AES	ICP	0.1 µg per 100 g of blood for Cu and Zn 0.2 µg per 1 g of tissue for Cu and Zn	$130

* See Appendix A for a list of the standard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Methods 8005 and 8310 from *NIOSH Manual of Analytical Methods* (NIOSH 1994) are recommended for detecting copper and zinc from blood/tissue and urine samples, respectively. Both methods are advantageous over other biological fluid

sampling methods in that they can be used to monitor both copper and zinc levels simultaneously from samples of blood/tissue or urine.

Procedures

Water, Soil, and Waste Samples — EPA Methods 7211 and 7951

Sample Collection, Transport, and Storage QA/QC

Collect samples in clean glass or polyethylene containers that have had the following cleaning treatment: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water. Acidify aqueous samples upon collection with HNO_3 to pH < 2; these may be stored at 4°C up to 6 months. Refrigerate solid samples (at 4°C) upon collection. These may be stored up to 6 months before analysis; however, it is recommended that samples be analyzed as soon as possible. These guidelines are provided in unattached Appendix N of this report (Chapter Three - Metallic Analytes, Section 3.1.3 - Sample Handling and Preservation, from EPA SW-846 [EPA 1995b]) and in unattached Appendix O of this report (EPA Methods 3015 and 3051, from EPA-SW-846 [EPA 1995b]).

Sample Preparation

EPA Method 3015 is recommended for sample preparation of aqueous samples and EPA Method 3051 is recommended for sample preparation of solid samples.

EPA Method 3015 — Microwave Assisted Acid Digestion of Aqueous Samples and Extracts.

This method involves digesting the collected samples (45 ml) with nitric acid (5 ml) and heating the mixture with microwave heat for 20 min. Before analysis, cool, filter, and centrifuge or allow the sample to settle.

EPA Method 3051 — Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils.

This method involves digesting the collected samples (0.5 g) with nitric acid (10 ml) and microwave heating for 10 min. Filter, centrifuge, and allow the sample to settle. Dilute the aqueous portion to an appropriate volume for furnace analysis.

Separation and Detection Parameters

1. Calibrate and set up the conditions of the atomic absorption spectrophotometer equipped with a graphite furnace as recommended by the manufacturer and by parameters listed in EPA Methods 7211 and 7951. (Correct for background absorption.)

2. Inject the sample into the furnace and dilute it if the concentration is greater than the highest standard concentration. Check standards after every ten samples. Perform quality control as described in EPA Method 7000A. Calibrate daily with standards and construct the resulting calibration curve. Analyze the working standard solution after every ten samples and determine recovery efficiency by spiking matrix samples with a known concentration of analyte.
3. Calculate and report results as µg of metal per liter of sample.

Equipment and Chemical List

1. Equipment:
   a. Atomic absorption spectrophotometer
   b. Burner
   c. Hollow cathode lamp
   d. Graphite furnace
   e. Graphical display and recorder
   f. Pressure reducing valves
   g. Pipettes and assorted glassware
   h. Microwave.
2. Reagents (all chemicals must be reagent grade):
   a. Concentrated nitric acid
   b. Concentrated hydrochloric acid
   c. High purity acetylene and nitrous oxide or argon
   d. Stock standard metal solutions
   e. Calibration standards (at least three)
   f. Reagent water.

Air Samples — NIOSH Method 7300

Sample Collection, Transport, and Storage QA/QC

1. Calibrate the sampling pump equipped with a cellulose ester membrane filter (0.8 µm pore size, 37 mm diameter, in cassette filter holder). Guidelines for air sample collection are provided in unattached Appendix N of this report (Section D - General Considerations for Sampling Airborne Contaminants, from the NIOSH Manual of Analytical Methods [NIOSH 1994]).
2. Sample the air at a flow rate of 1 to 4 L/min (for a minimum volume of 5 L and a maximum volume of 1000 L for copper and 5 to 200 L for zinc). Take two to four replicate samples.
3. Immediately after sampling, tighten the filter holder tubes and place them in suitable containers for shipment to the lab as soon as possible. Label the filter holder tubes with pertinent information including time of collection, temperature, humidity, and atmospheric pressure.

Sample Preparation

1. Transfer the filter (sample) from the cassette filter holder to a clean beaker and add 5 ml of ashing acid. Cover with a watchglass and incubate at room temperature for 30 min. (Reagent blanks can also be started at this time.) Heat the sample on a hot plate (120°C) to near dryness until the volume has been reduced to 0.5 ml.
2. Extract the sample multiple times with ashing acid (2 ml) and heat until the solution is clear. Perform all acid digestions under a well ventilated hood.
3. Rinse the beaker containing the sample with water and heat (150°C) to near dryness. Dissolve the residue with 2 to 3 ml of dilution acid. Transfer the sample to a 10-ml volumetric flask and dilute to volume with dilution acid.

Separation and Detection Parameters

1. Set and calibrate the spectrometer's conditions according to the manufacture's recommendations. The wavelength for copper is 324.8 nm and 213.9 nm for zinc. Also calibrate with an acid blank and 10 µg/L of multi-element working solution in 4% HNO_3 and 1% $HClO_4$ containing copper and zinc.
2. Analyze samples and standards. Dilute samples with dilution acid if the sample readings are above standard readings.
3. Calculate and report the concentration of the analyte (mg/m^3).
4. Analyze standards for every ten samples and check the recovery for two spiked media blanks per ten samples.

Equipment and Chemical List

1. Equipment:
   a. Personal sampling pump with a cellulose ester membrane (0.8 µm pore size, 37 mm diameter, in cassette filter holder)
   b. Spectrometer equipped with
      -inductively coupled plasma-atomic emission
      -two stage regulator
      -argon gas
   c. Hotplate , surface temperature 150°C
   d. Assorted glassware (i.e., beakers, watchglass covers, flasks) and pipettes.
2. Reagents:
   a. Acids — ultra pure and concentrated: nitric acid and perchloric acid
   b. Ashing acid — HNO_3:$HClO_4$, 4:1 (v:v)
   c. Dilution acid — 4% HNO_3, 1% $HClO_4$ (add 50 ml of ashing acid to 600 ml of water, then dilute with water to a final volume of 1 L)
   d. Calibration stock solutions — 1000 µg/ml of commercially prepared solution containing titanium
   e. Distilled, deionized water.

Urine Samples — NIOSH Method 8310

Sample Collection, Transport, and Storage QA/QC

Collect urine (50 ml) and preserve with 5 ml of HNO_3 in a polyethylene bottle. Pack the sample in an insulated container and ship under refrigeration. Guidelines for collecting biological samples are provided in unattached Appendix N of this report (Section F - Special Considerations for Biological Samples, *NIOSH Manual of Analytical Methods* [NIOSH 1994]).

Sample Preparation

1. Extract the analyte(s) from urine with polydithiocarbamate resin (60 mg) at pH 2.0 and shake for 12 hr.
2. Filter the sample; re-extract filtrate with more resin. Combine the collected resin and filter from the two extractions.
3. Perform an acid digest (similar to the one described in Method 7300) on the collected resin and filter.
4. Dissolve the residue in 2 to 3 ml of digestion acid and dilute to a volume of 5 ml with deionized water.

Note: Take an aliquot of the urine sample to determine the creatinine level.

Separation and Detection Parameters

1. Set and calibrate the spectrometer according to the manufacture's recommendations. The wavelength for copper is 324.8 nm and 213.9 nm for zinc. Also calibrate with an acid blank and 10 µg/L of multi-element working solution in 4% HNO_3 and 1% $HClO_4$ containing copper and zinc.
2. Analyze the standards and samples. If the sample readings are above the range of the standards, dilute the samples with 1 volume digestion acid plus 9 volumes of deionized water.
3. Calculate the concentration of analyte (mg/m^3) but report the results as µg of metal per g of creatinine.
4. After every ten samples, analyze standards and check recovery measurements with spiked urine samples (3) from individuals in a control group (unexposed people).

Equipment and Chemical List

1. Equipment:
   a. Spectrometer equipped with
      -inductively coupled plasma-atomic emission
      -two stage regulator
      -argon gas
   b. Hotplate, surface temperature 100°C

c. Filtering apparatus for 50 ml liquid (47 mm cellulose ester, 0.8 µm pore size filters)
d. pH meter and electrodes
e. Mechanical shaker
f. Assorted glassware (i.e., beakers, watchglass covers, flasks) and pipettes. Polyethylene bottles - 125 or 250 ml. All labware must be detergent washed, soaked 12 hr in 10% (v/v) HNO_3, and soaked 12 hr in deionized water.

2. Reagents:
   a. Polydithiocarbamate resin
   b. Acids — ultra pure and concentrated: nitric acid and perchloric acid
   c. Dilution acid, 4% HNO_3, 1% $HClO_4$ (add 50 ml of ashing acid to 600 ml of water), then dilute with water to a final volume of 1 L
   d. Sodium Hydroxide, 5 M (dissolve 20 g of NaOH in 50 ml boiled, deionized water, and then dilute to 100 ml. Dilute again to a final volume of 1 L)
   e. Metal standards — 1000 µg/ml of commercially prepared solution containing copper and zinc
   f. Distilled, deionized water.

Blood and Tissue Samples — NIOSH Method 8005

Sample Collection, Transport, and Storage QA/QC

Collect blood (dry tissue weight of 0.25g or wet tissue weight of 1 g) in tubes containing heparin; mix and freeze until use. Guidelines for collection of biological samples are provided in unattached Appendix N of this report (Section F - Special Considerations for Biological Samples, from the *NIOSH Manual of Analytical Methods* [NIOSH 1994]).

Sample Preparation

1. Digest samples with 10 ml of digestion acid/10 g of blood, 5 ml of digestion acid to wet (1 g) or dry (0.25 g) tissue. Heat at 110°C for 2 hrs.
2. Increase temperature to 250°C and heat until the volume has been reduced to 1 ml for blood samples and 0.5 ml for tissue samples.
3. Transfer samples to volumetric flasks: 10 ml flask for blood and 5 ml flask for tissue. Bring the flasks to volume with water.

Separation and Detection Parameters

1. Set and calibrate the spectrometer according to the manufacture's recommendations. The wavelength for copper is 324.8 nm and 213.9 nm for zinc. Also calibrate with an acid blank and 10 µg/L of multi-element working solution in 10% H_2SO_4 containing copper and zinc.

2. Analyze standards and samples. If the sample readings are above the range of standards, dilute samples with 10% H_2SO_4.
3. Calculate and report concentration of analyte (µg of analyte per g of blood or tissue).
4. After every ten samples, analyze standards and check recovery measurements with spiked blood samples (3) from unexposed people. Correct for background metal levels by subtracting the value of the unspiked from the spiked samples.

Equipment and Chemical List

1. Equipment:
   a. Spectrometer equipped with
      -inductively coupled plasma-atomic emission
      -two-stage regulator
      -argon gas
   b. Blood collection tube with heparin and 21-gauge needles
   c. Gloves, knives, forceps, alcohol
   d. Hotplate - 110 to 250°C
   e. Mechanical shaker
   f. Assorted glassware (i.e., beakers, watchglass covers, flasks) and pipettes; Polyethylene bottles - 125 or 250 ml.
2. Reagents:
   a. Acids — ultra high purity and concentrated: nitric, perchloric, and sulfuric.
   b. Digestion acid — HNO_3:$HClO_4$:H_2SO_4, 3:1:1 (v:v:v)
   c. Yttrium standard, 5 µg/ml in 5% HNO_3; combine 50 ml of HNO_3 to 500 ml water and 5 ml of 1000µg Y/ml standard; dilute to 1 L with water
   d. Metal standards — 1000 µg/ml of commercially prepared solution containing copper and zinc
   e. Distilled, deionized water.

4 Fog Oil

Use and Properties

Fog oil is a low-viscosity petroleum oil used by the military to generate screening smokes (Kroschwitz and Howe-Grant 1993). The fog (or smoke) is generated by evaporating the hydrocarbons in the oil. Historically, the two major components of fog oil were aliphatic and aromatic hydrocarbons with traces of alcohol, organic acids, esters, and metals (Katz et al. 1980). Then in 1986, a new military specification for fog oil was implemented that required the removal of carcinogenic compounds in the oil (Brubaker, Rosenblatt, and Synder 1992). Fog oil is still composed of many different types of chemicals but the predominant class of chemicals are aliphatic hydrocarbons with very low levels of non-carcinogenic aromatic hydrocarbons (Brubaker, Rosenblatt, and Synder 1992). Table 4-1 lists some common properties of fog oil.

Table 4-1. Chemical and physical properties of fog oil.

Chemical Name	Petroleum
Synonyms	Crude oil Gasoline Smoke generating fuel
CAS Registry Number	
Molecular Formula	
Molecular Weight	mean 300 lb/lb-mole
Physical Description	Dark yellow to brown, oily liquid
Density	0.83 to 0.93 gm/ml
Melting Point	371^{o}C

Possible Methods

Standard Methods

Standard analytical methods for aliphatic hydrocarbons, total petroleum hydrocarbons, waterborne oil, and total oil are listed in this chapter. Standard methods for aromatic and polycyclic aromatic hydrocarbons are also included since

aromatic and aliphatic hydrocarbons were the major components of fog oil prior to 1986.

In *Annual Book of ASTM Standards*, Vol. 11.02 (ASTM 1994):

Method D3650-93 — This method uses fluorescence analyses to identify waterborne petroleum oils.

Method D3328-90 — This method analyzes waterborne petroleum oils by GC equipped with a packed column or capillary column.

Method D5037-90 — This method uses the HPLC to determine the waterborne petroleum oils.

Method D3414-80 — Infrared (IR) spectroscopy is used to determine waterborne petroleum oils.

Method D5412-93 — Fluorescence spectroscopy is used to determine PAH mixtures in water.

In *Annual Book of ASTM Standards*, Vol. 11.02 (ASTM 1993):

Method D4281-92 — This gravimetric method determines oil and grease in water and wastewater.

Method D3921-85 — This method determines oil, grease, and petroleum hydrocarbons in water by using IR spectroscopy.

Method D4657-92 — This method determines PAH in water by HPLC.

In *Standard Methods for the Examination of Water and Wastewater* (APHA 1992):

Method 5520B-E — This method offers various tests for determining total oil and hydrocarbons in water and sludge. The techniques include gravimetric, IR spectroscopy, and Soxhlet methods.

Methods 6440B and C — Method B is very similar to Method D4657-92. It uses the HPLC with a fluorescence or UV detector to identify unknown PAHs in water. Method C uses the GC/MS with an FID detector to detect higher concentrations of PAH from water or wastewater.

Method 6220B-E — This method describes several ways to extract the volatile aromatic organics and identify them using GC or GC/MS.

In *Test Methods for Evaluating Solid Waste*, EPA SW-846 (U.S. EPA 1995b):

Method 4030 — Screens for total petroleum hydrocarbons in soil by using immunoassay techniques. (This method was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).

Method 4035 — Screens for PAHs in soil (> 1 mg/kg) by using immunoassay methods. (This method was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).

Method 8015A — This GC method measures nonhalogenated volatile organics, including petroleum hydrocarbons, by FID detection in water, solid, and waste mediums. (This method has been revised and was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).

Method 8100 — This GC method measures certain PAHs in solid waste and wastewater using both packed and capillary columns.

Method 8260B — A GC/MS method for detecting volatile organic compounds in soil, water, and waste matrices with capillary column technique. (This method has been revised and was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).

Method 8270C — Semivolatile organic compounds (including PAHs) in soil, waste material, and groundwater are identified by GC/MS using a capillary column. (This method has been revised and was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995). Analysis for polyaromatic hydrocarbons in fog oil (Driver, et al. 1993) was performed recently based on EPA Method 8270C (located in unattached Appendix C).

Method 8310 — This method determines the concentration of PAHs from soil, groundwater and waste by using the HPLC.

Method 8410 — This method uses GC/FT-IR spectrometry to determine semivolatile organics in soil and sediments, wastewater, and solid waste.

Method 8440 — IR spectrophotometric method with supercritical CO_2 extraction in determining nonvolatile total petroleum hydrocarbons from soil, sediment, and sludge samples. (This method was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).

Method 8275A — Used in qualitatively screening semivolatile organic compounds from nonaqueous solid wastes and soils by using TC/MS. (This method has been revised and was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).

Methods 9070 and 9071A — These methods measure oil and grease from water, wastewater, and sludges using gravimetric methods.

In *Methods for the Determination of Organic Compounds in Drinking Water,* EPA-600/4-88/039, EPA-600/4-90/020 (Supplement 1), and EPA-600/R-92/129 (Supplement 2) (EPA 1991a):

Method 502.2 — Measures purgeable volatile organic compounds in raw and finished water by using capillary column GC with photoionization and electrolytic conductivity detectors.

Method 524.1 — Measures purgeable organic compounds in raw and finished water with a packed column GC/MS.

Method 524.2 — Measures purgeable organic compounds in surface, ground, and finished water by capillary column GC/MS.

Method 525.1 — This method uses liquid-solid extraction and capillary column GC/MS to measure organic compounds in raw and finished water.

Methods 550 and 550.1 — Both methods measure PAH in drinking water with HPLC coupled to UV and fluorescence detector. The extraction step in Method 550 involves liquid-liquid extraction; Method 550.1 uses liquid-solid extraction.

In *Methods for Chemical Analysis of Water and Wastes,* EPA-600/4-79-020 (EPA 1983):

Methods 413.1 and 413.2 — Measure total recoverable grease and oil (non-volatile hydrocarbons) from surface and saline waters, and industrial and domestic wastes by using gravimetric and IR spectrophotometric methods, respectively.

Method 418.1 — Measures total recoverable petroleum hydrocarbons from saline and surface waters, and industrial and domestic waste by IR spectrophotometric methods.

In *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,* EPA-600/4-89-017 (EPA 1988):

Method TO1 — Uses Tenax GC adsorption and GC/MS techniques to determine volatile organic compounds (with boiling ranges between 80 and 200°C) in ambient air.

Method TO2 — Uses carbon molecular sieve adsorption and GC/MS methods to determine highly volatile organics (with boiling ranges between -15 and 120°C) in ambient air.

Method TO3 — Uses cryogenic trapping with GC-FID or electron capture detector (ECD) to determine volatile organics (with boiling ranges between -10 and 200°C) in ambient air.

Method TO13 — PAH determination in ambient air by GC and HPLC methods.

Method TO14 — Determination of volatile and semivolatile organic compounds in ambient air by using GC equipped with various nonspecific and specific detectors

In *NIOSH Manual of Analytical Methods* (NIOSH 1994):

Methods 5506 and 5515 — Both methods determine PAH in air. Method 5506 uses HPLC with fluorescence/UV detection. Method 5515 uses GC with a capillary column and an FID detector.

Method 5026 — This method uses IR spectroscopy to detect oil mists in air.

Method 1501 — This method uses GC-FID to determine aromatic hydrocarbons in air.

Method 1500 — This method measures hydrocarbons (boiling point ranges 36 to 126°C) in air by GC-FID.

In *Official Methods of Analysis of AOAC International* (AOAC 1995):
Method 973.30 — Measures PAH in food products by using spectrophotometric methods.

Nonstandard Methods

The following nonstandard methods specifically measure for fog oil in soil and plant samples.

"Environmental effects of fog oil and CS usage at the Combat Maneuver Training Center, Hohenfels, Germany" (Brubaker, Rosenblatt, and Synder 1992):

> This report describes methods for field sampling as well as detection methods for fog oil and CS in soil and plant samples. Fog oil was initially identified by GC-MS and environmental samples were screened by GC-FID methods.

"Evaluation and characterization of mechanisms controlling transport, fate, and effects of army smokes in an aerosol wind tunnel. Transport, transformations, fate, and terrestrial ecological effects of fog oil obscurant smokes" (Cataldo et al. 1989):

> This report compares several detection methods including IR, GC, and HPLC for measuring fog oil from plant samples. Less plant hydrocarbon interferences were observed when the HPLC with UV detection method was used. However, the actual detection procedures were not adequately described.

Development Trends

Abiotic Media

Due to the complex nature of petroleum, group-type analysis of a given mixture is being used to separate out or isolate the desired compounds. Standard and nonstandard analytical methods for oil analysis in abiotic mediums use GC, GC/MS, IR, or HPLC techniques with an array of extraction methods ranging from solid phase extraction to adsorption chromatography on adsorbents (Wang, Fingas, and Li 1994; Akhlaq 1993). For quick identification of oil contamination, an immunoassay for screening petroleum hydrocarbons in soil has recently been promulgated in *Test Methods for Evaluating Solid Waste,* EPA SW-846 (EPA 1995b). Most of these standard methods are listed in the previous section (Possible Methods).

Biotic Media

Analytical methods that specifically assayed for fog oil in biological fluids such as blood or urine were not identified. However, a nonstandard GC-MS method for measuring kerosene in blood was reported by Kimura et al. (1991). Analytical methods using GC-MS and GC for measuring kerosene and diesel fuel in shellfish and fish tissues were also identified (Farrington et al. 1982; Newton, Rothman, and Walker 1991). These methods were not listed in the section titled "Possible Methods" since components of kerosene and diesel fuel consist of much lighter and heavier hydrocarbons that are not normally found in the newer refined fog oil.

Recommended Methods

The standard methods recommended in this section describe analytical processes for determining total petroleum oil/hydrocarbon rather than specific moieties of oil. These methods are useful in rapidly identifying petroleum contamination. The recommended nonstandard method specifically assays for fog oil.

Standard Methods

Table 4-2 lists a brief summary of recommended standard methods for fog oil analysis. EPA Method 4030 from EPA SW-846 (EPA 1995b) is an immunoassay for detecting total petroleum hydrocarbon (TPH) in soil. This screening method is ideal for testing soil samples suspected of being contaminated with petroleum. This assay is relatively simple to use; results may be obtained within an hour of sampling. The immunoassay kit, which is available commercially, contains all necessary reagents and apparatus to successfully perform the assay. This method will not distinguish fog oil from other petroleum contaminants.

Method 5026 from *NIOSH Manual of Analytical Methods* (NIOSH 1994) is an IR spectrophotometry method and is recommended for assaying oil mists (such as mineral oil mist) in air. The working range for this method is 1 to 20 mg/m^3 for a 100-Liter air sample and is applicable to all trichlorotrifluoroethane-soluble oils. Fog oil mist is categorized as a subset of mineral oil mist (Brubaker, Rosenblatt, and Synder 1992).

APHA Method 5520C from *Standard Methods for the Examination of Water and Wastewater* (APHA 1992), which uses IR spectrophotometry, is recommended to detect the presence of oil (that is soluble in trichlorotrifluoroethane) in water or

wastewater. The method is similar to NIOSH Method 5026 with the exception of the sampling matrix.

Table 4-2. Recommended standard methods for fog oil analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Soil	collect samples in glass container and store at 4°C	follow extraction procedures in commercial kit	spectrophotometer	optical density (OD) measurements	greater than 25 ppm in soil	$25 per test
Air	after air sampling, remove filter holder and cap tightly, place in a suitable container and ship to the lab as soon as possible	extract sample filters with 10 ml of trichlorotrifluoroethane	spectrometer	infrared	0.05 µg per sample	$100
Water and waste sludge	Collect sample and acidify with HCl (1:1) to pH 2 or lower and refrigerate	extract sample with trichlorotrifluoroethane	spectrometer	infrared	can be as low as 0.2 mg per volume of sample	$50

* See Appendix A for a list of the standard methods

** Estimated total analysis cost, including sample preparation, per sample.

Nonstandard Methods

The nonstandard method by Brubaker, Rosenblatt, and Synder (1992) is recommended for field screening of fog oil in soil and plant samples. While both of the nonstandard methods listed in the section titled “Possible Methods” specifically assayed for fog oil and use very sophisticated equipment, the overall method by Brubaker, Rosenblatt, and Synder (1992) was better described. They provided very detailed methods for sample collection, sample preparation, and analyte detection. However, the report by Cataldo et al. (1989) provided useful information regarding HPLC detection of fog oil and should be used as a guideline for developing or further investigating HPLC methods for determining fog oil from both abiotic and biotic mediums. Table 4-3 lists a brief summary of the recommended nonstandard method for fog oil analysis.

Table 4-3. Recommended nonstandard method for fog oil analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Plant	collect plant samples and mix until homogeneous, then transfer to clean 250 ml sample bottle	solvent extraction followed by concentration with K-D apparatus	GC	FID	not provided	$450
Soil	collect soil samples and mix until homogeneous, then transfer to clean 250 ml sample bottle	solvent extraction followed by concentration with K-D apparatus	GC	FID	5 ppm 30 g of soil	$450

* See Appendix B for a list of the nonstandard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Procedures

Soil Samples — EPA Method 4030

Sample Collection, Transport, and Storage QA/QC

Collect all samples in a wide-mouthed glass container with a teflon-lined lid. Store samples at 4°C. Extract samples within 14 days of collection and analyze the extracts within 40 days of extraction. These guidelines are provided in unattached Appendix N of this report (Chapter Four - Organic Analytes, Section 4.1 - Sampling Considerations, from EPA SW-846 [EPA 1995b]).

Sample Preparation

Follow soil extraction procedures as described in the commercially available test kit.

Separation and Detection Parameters

1. Add an aliquot of the sample extract to the TPH-antibody mixture along with an enzyme-TPH conjugate reagent. Both the conjugate reagent and the hydrocarbon present in the sample extract compete to bind to the TPH-antibody. The response produced by the sample is compared to the response made by a standard reaction.
2. Follow the quality control procedures as specified in the test kit in addition to the following precautions: (1) do not use test kits past their expiration date; (2) use tubes and reagents specified for that test only; and (3) use test kits within the specified storage and operating temperature.

Equipment and Chemical List

All commercially purchased immunoassay kits supply the apparatus and materials needed for successful completion of the test. Some of the commercially available kits are from companies such as EnSys, Inc. (PETRO RISc Soil Test) and Millipore, Inc. (EnviroGard™ Petroleum Fuels in Soil).*

Air Samples — NIOSH Method 5026

Sample Collection, Transport, and Storage QA/QC

1. Calibrate the sampling pump with a polyvinyl chloride (PVC) or mixed cellulose ester (MCE) membrane filter (37-mm, 0.8 or 5 µm pore size, two-piece filter cassette). Guidelines for air sample collection are provided in unattached Appendix N of this report (Section D - General Considerations for Sampling Airborne Contaminants, from the *NIOSH Manual of Analytical Methods* [NIOSH 1994]).
2. Sample 20 to 500 L of air at a rate of 1 to 3 L/min. Take 2 to 4 replicate samples and 2 to 10 field blanks per set.
3. Immediately after sampling, place tightly capped filter holder tubes in suitable containers and ship to the lab as soon as possible. Label the filter holder tubes with pertinent information including time of collection, temperature, humidity, and atmospheric pressure.

Sample Preparation

1. Carefully transfer sample filters and blank filters into vials and extract with 10 ml of trichlorotrifluoroethane by shaking vigorously.
2. Determine the recovery efficiency for every lot of filters by spiking filters with known concentrations of standards. Store the filters overnight after the solvent has evaporated. After the extraction process, scan the extract and calculate the amount of recovered oil.

Separation and Detection Parameters

1. Calibrate the infrared spectrophotometer with at least six working standards in the range of 5 to 250 µg/ml and generate a calibration curve.
2. Scan each sample or blank filter extract from 3200 to 2700 cm^{-1} in absorbance mode vs. trichlorotrifluoroethane in the reference beam. Record the largest absorbance reading near 2940 cm^{-1}.

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* Listing of manufacturer/supplier names does not constitute endorsement by the Federal government or the U.S. Army.

3. Calculate and report the concentration of oil in the volume of sampled air (in mg/m^3).
4. Routinely scan standards between sample measurements.

Equipment and Chemical List

1. Equipment:
   a. Infrared spectrophotometer with scanning capability in the 3200 to 2700 cm^{-1} region and infrared quartz cells
   b. Sampling pump with PVC or MCE membrane filter
   c. Assorted glassware (i.e., vials, flasks, pipettes) and tweezers.
2. Reagents:
   a. Trichlorotrifluoroethane ($C_2Cl_3F_3$)
   b. Stock oil standard - 20 mg/ml.

Water and Waste Sludge Samples — APHA Method 5520C

Sample Collection, Transport, and Storage QA/QC

Collect water sample in a clean wide-mouthed glass container, acidify with HCl (1:1) to pH 2 or lower, and refrigerate until use. Preserve sludge samples with 1 ml of HCl per 80 g of sample and refrigerate until use. Guidelines for sample collection can be found in unattached Appendix E of this report (Method APHA 5520C *Standard Methods for the Examination of Water and Wastewater* [APHA 1992]).

Sample Preparation

1. Extract and separate oil from the sample with trichlorotrifluoroethane (30 ml) and shake vigorously.
2. Drain the trichlorotrifluoroethane layer (bottom layer) through a funnel lined with filter paper and 10 gm of sodium sulfate. If a clear solvent is not obtained, transfer to a centrifuge tube and spin at 2400 rpm for 5 min. Repeat this step until a clear solvent is obtained.
3. Combine all extracts and bring to a volume of 100 ml with the solvent.
4. Make standard oil solutions (two or more) in concentrations within the range of interest.
5. Determine recovery efficiency by analyzing samples with known levels of analyte(s).

Separation and Detection Parameters

1. Calibrate the infrared spectrophotometer with at least three standard oil solutions with concentrations within the range of the sample readings.
2. Scan samples, standards, and blanks from 3700 to 2700 cm^{-1} with the solvent as the reference beam. Record absorbance reading at 2930 cm^{-1}.

3. Record absorbance; calculate and report concentration of oil per volume of sample (in mg/L).
4. Make daily calibrations with at least three different levels of standard solutions (low, mid, and high). Daily verify standards within the linear range.

Equipment and Chemical List

1. Equipment:
   a. Infrared spectrophotometer with double beam recording and near-infrared silica cells.
   b. Centrifuge and 100 ml centrifuge tubes (glass)
   c. Separatory funnels, liquid funnels, volumetric flasks, and filter paper.
2. Reagents:
   a. Trichlorotrifluoroethane
   b. Hydrochloric acid
   c. Sodium sulfate
   d. Reference standard: isooctane (37.5%), hexadecane (37.5%), benzene (25%).

Plant and Soil Samples — Brubaker et al. (1992)

Sample Collection, Transport, and Storage QA/QC

Plant samples: Mark a circle measuring approximately 10 m in diameter in the center of the sampling location. Using precleaned stainless steel scissors, collect 8 to 10 grab samples of vegetation consisting of grass blades, leaves from trees or shrubs, or needles from conifers. Roots, stems, or twigs should not be included in these samples. Place collected samples in a stainless steel tray lined with aluminum foil and mix thoroughly. Enough samples should be collected to fill a clean 250 ml glass sample bottle. Wipe sample bottles clean of any outside debris and label properly. Place samples in a cool container for transport.

Soil samples: Mark a square measuring approximately 10 m (per side) in the center of the sampling location. Pull vegetation from a square measuring approximately 8 cm (per side) before soil collection. Using a precleaned stainless steel spoon, take soil samples from the 8-cm square area to a depth of 4 cm. Place the collected samples in a stainless steel tray lined with aluminum foil and thoroughly mix. Place the homogeneously mixed soil samples in a precleaned, 250-ml glass sample bottle until it is full. Discard the remaining samples. Wipe sample bottles clean of debris and labeled. Take five grab samples along with duplicates from one location.

Sample Preparation

Plant samples: Weigh plant samples and place in a beaker with 30 g of sodium sulfate. (Extract the sodium sulfate with hexane and acetone before use). Add

200 ml of hexane to the beaker and store overnight at 4°C. Sonicate the plant samples for 3 min with a sonic cell disrupter. Filter the solvent extract through Whatman #41 filter paper by using a Buchner funnel connected to a vacuum. Repeat this procedure twice using two additional 200-ml portions of hexane. Concentrate the samples using the Kuderna-Danish (K-D) apparatus. Pour the extract into a 500-ml evaporating flask and immerse in a hot water bath until the volume decreases to 1 ml. Upon cooling, add hexane to bring the volume to 10 ml. Transfer the extract to a teflon-sealed centrifuge tube and store at 4°C until analysis.

Soil samples: Place 30 g of soil in a beaker with 30 g of sodium sulfate (that has been previously extracted with hexane and acetone). Add 100 ml of 1:1 methylene chloride:acetone to the sample beaker and store overnight at 4°C. Sonicate soil samples for 3 min with a sonic cell disrupter. Filter the extract through Whatman #41 filter paper by using a Buchner funnel connected to a vacuum. Repeat this procedure twice using two additional 100-ml portions of 1:1 methylene chloride:acetone. Concentrate the samples and store as described above in the section on plant sample preparation.

Separation and Detection Parameters

1. Set the GC-FID system with the following operating conditions:

Parameter	Setting
Injector temperature	270°C
Injector volume	3 µl
Detector temperature	290°C
Initial temperature	100°C
Initial time	2 min
Temperature and end of the first ramp	120°C
Ramp rate 1	5°C/min
Final temperature	320°C
Ramp rate 2	12°C/min
Final time	10 min
Total run time	25 min
Carrier gas-Helium velocity	19 cm/s

2. Calibrate the GC with at least 5 calibration standards (11.52 through 576 ng/µl) and plot the response factor to determine the detector response range.
3. Analyze samples as well as matrix spikes and duplicates. Analyze standards at the beginning, after every 10 samples, and at the end of the run.

4. Since fog oil is composed of many different types of hydrocarbons, integrate the entire envelope (composed of many peaks) as a single peak. When analyzing the data, apply a ratio and subtraction technique (via Nelson Analytical Software 2500 Series Chromatography Data System, Rev.5.0*) to cancel baseline drifts and to eliminate elution patterns resembling fog oil patterns.

Equipment and Chemical List

1. Equipment:
   a. GC with an FID detector and equipped the following items:
      - capillary column (J&W DB-5, 30 m x 0.32 mm ID, 0.25 µm)
      - autosampler injection system
      - splitless injection port
      - Nelson Analytical Software 2500 Series Chromatography Data System, Rev. 5.0, for data processing
      - gases- helium, hydrogen, and air
   b. K-D apparatus
   c. Sonic cell disrupter
   d. Mettler balance
   e. Hot water bath
   f. Miscellaneous laboratory equipment: flasks, beakers, stainless steel utensils, sampling bottles, funnels, filter paper, centrifuge tubes.
2. Reagents:
   a. Methylene chloride
   b. Acetone
   c. Hexane
   d. Sodium sulfate
   e. Calibration standards
   f. Spiking standards
   g. Fog oil (pure).

* Listing of company name and software does not constitute endorsement by the Federal government or the U.S. Army.

5 Graphite

Use and Properties

The military application of graphite flakes or powder is as an obscurant to screen electromagnetic tracking and targeting systems (Driver et al. 1993). Graphite flakes perform well in obscuring mid and far infrared (IR) bands as well as a combination of visible, near-IR, mid-IR, and far-IR bands (Palmer 1992). Graphite, a soft-scale form of carbon, exists naturally and synthetically and is chemically inert. Besides being used as an obscurant by the military, the synthetic form of graphite is also used commercially in lubricants, electrodes, "lead" pencils, and foundry facing (Driver et al. 1993). Graphite is considered a "nuisance dust" to humans by the American Conference of Governmental Industrial Hygienists (ACGIH) and is overtly toxic. Inhalation of graphite exceeding the threshold limit value (TLV) of 10 mg/m^3 is associated with pneumoconiosis in graphite workers (Driver et al. 1993). Table 5-1 lists some common properties of graphite.

Table 5-1. Chemical and physical properties of graphite.

Chemical Name	Graphite
Synonyms	Mineral Carbon Black Lead Carbofilm Plumbago
CAS Registry Number	7782-42-5
Molecular Formula	C
Molecular Weight	12
Physical Description	Black, greasy, odorless solid
Density	2.25 g/ml
Melting Point	3337.7^{o}C

Possible Methods

Standard Methods

Due to the nonhazardous/pollutant status of graphite, no standard analytical method(s) specifically for graphite have been identified. Graphite is not considered a hazardous waste/substance under the Resource Conservation and Recovery Act (RCRA) or the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Graphite is not a regulated pollutant as stated by the Clean Air Act (CAA), but is regulated for 24-hr particulate air concentration. The Clean Water Act also does not have a standard discharge concentration for graphite (Driver et al. 1993). However, a gravimetric method for detecting carbon black as an airborne particulate material is described in NIOSH Method 5000 (NIOSH 1994). This method may be used to determine graphite particulate concentrations in air.

Development Trends

Abiotic Media

Analytical methods for quantitating graphite in abiotic mediums such as soil, water, and air were not identified. However, physical measurements (such as diameter and thickness) of graphite particles or flakes have been determined by scanning electron microscopy (SEM) in test materials collected from studies involving inhalation toxicity of graphite dust (Aranyi et al. 1992, Ligotke et al. 1989, Thomson et al. 1988). Aranyi et al. (1992) also briefly mentions a gravimetric method to quantify graphite from air samples. Method development is needed to fully assess graphite contamination in abiotic mediums.

Biotic Media

No analytical methods for detecting graphite in biotic mediums such as blood, urine, and animal and plant tissues have been identified. There are numerous inhalation toxicological studies of graphite dust in rats, but none of these studies actually assay for graphite in tissues, blood, or urine. Methods for detecting graphite in biotic mediums also need to be investigated.

Recommended Methods

Method 5000 from *NIOSH Manual of Analytical Methods* (NIOSH 1994) for detecting carbon black as airborne particulate is recommended as a field method for detecting graphite from air. This method is not ideal since it does not specifically assay for graphite; any airborne particulate may result in a false positive response. However, if graphite flakes are known or suspected to be the contaminant, this method may be used to determine the concentration in air. Table 5-2 lists a recommended standard method for graphite analysis.

Table 5-2. Recommended standard method for graphite analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Air	weigh filter before sampling and ship the tightly capped filter holder tube in an appropriate container	equilibrate filter cassette to balance room environment prior to weighing	PVC filter	gravimetric (filter weight)	0.03 mg per sample	$100

* See Appendix A for a list of the standard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Procedures

Air Samples — NIOSH Method 5000

Sample Collection, Transport, and Storage QA/QC

1. Before sampling, equilibrate filters in an environmentally controlled weighing area for at least 2 hours and weigh (static-free). Calibrate the sampling pump with the representative sampler in line. Guidelines for air sample collection are provided in unattached Appendix N of this report (Section D - General Considerations for Sampling Airborne Contaminants, from the *NIOSH Manual of Analytical Methods* [NIOSH 1994]).
2. Collect a total volume of 30 to 570 L at a rate of 1 to 2 L/min. Take an additional 2 to 4 replicate samples for each batch of field samples for quality assurance on the sampling procedure.
3. Immediately after sampling, place tightly capped filter holder tubes in suitable containers and ship to the lab as soon as possible. Label the filter holder tubes with pertinent information including time of collection, temperature, humidity, and atmospheric pressure.

Sample Preparation

1. Wipe the filter cassettes free of dust and remove plugs.
2. Equilibrate the filter cassettes to balance room environment for at least 2 hrs.
3. Carefully remove the filter and place it on the microbalance.

Separation and Detection Parameters

1. Zero the microbalance and calibrate with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights. Use the sample balance for weighing filters before and after sample collection.
2. Weigh sample filters and field blanks and record the post-sampling weights.
3. Calculate and report concentration of analyte (milligrams of analyte per cubic meter of sampled air).

Equipment List

1. Equipment:
   a. Personal sampling pump equipped with a PVC filter (37-mm, 5 µm pore size) and a stainless steel support screen in 37-mm
   b. Cassette filter holder (preferably conductive)
   c. Microbalance capable of weighing to 0.001 mg
   d. Static neutralizer and forceps.

6 Hexachloroethane

Use and Properties

In addition to use by the military as a smoke-producing munition, hexachloroethane is used commercially as a precursor in the production of fluorocarbons, and as an ingredient in some lubricants, fungicides, insecticides, moth repellents, plastics, veterinary medicines, and cellulose (Smith-Simon and Donohue 1994; Gordon, Hartley, and Roberts 1991). As a munition, hexachloroethane is mixed with zinc oxide and aluminum for use in devices such as smoke pots, grenades, and projectiles (Department of Army 1974). Table 6-1 lists some common properties of hexachloroethane.

Table 6-1. Chemical and physical properties of hexachloroethane.

Chemical Name	Hexachloroethane
Synonyms	HC HCE 1,1,1,2,2,2-Hexachloroethane Carbon hexachloride Carbon trichloride Perchloroethane Distopan (trade name) Egitol (trade name)
CAS Registry Number	67-72-1
Molecular Formula	C_2Cl_6
Molecular Weight	236.76
Physical Description	colorless to yellowish-white, solid
Density	2.091 g/ml at 20°C
Melting Point	185°C, sublimes at 187°C

Possible Methods

Standard Methods

Hexachloroethane is on the EPA Priority Pollutant List and Target Compound List. Hexachloroethane is listed as an analyte in the following standard methods.

In *Standard Methods for the Examination of Water and Wastewater* (APHA 1992):

Method 6410 B — For Extractable Base/Neutral and Acids by Liquid-Liquid Extraction Gas Chromatographic/Mass Spectrometric Method (Equivalent to EPA Method 8121). Hexachloroethane is classified as a base/ neutral extractable.

In *Test Methods for Evaluating Solid Waste*, EPA SW-846 (EPA 1995b):

Method 8121 — Determines chlorinated hydrocarbons including hexachloroethane by GC with electron capture detection in extracts of soil, waste, and groundwater.

Method 8260B — Determines volatile organic compounds (including hexachloroethane) by GC/MS with capillary column technique in extracts of soil, waste, and groundwater. (This method has been revised and was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995).

Method 8270C — Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary column GC technique for the determination of semivolatile organic compounds (including hexachloroethane) in extracts of solid waste matrices, soils, and ground water. (This method has been revised and was announced for public comments in the Federal Register on July 25; the comment period ended on September 25, 1995.

Method 8410 — Determines semivolatile organic compounds (including hexachloroethane) in wastewater, soils and sediments, and solid wastes using GC/FT-IR spectrometry.

In *Methods for the Determination of Organic Compounds in Drinking Water* (EPA 1991):

Method 524.2 — Measures purgeable organic compounds (including hexachloroethane) in water by capillary column GC/MS.

In *NIOSH Manual of Analytical Methods* (NIOSH 1994):

Method 1003 — For the determination of halogenated hydrocarbons in air by GC-FID.

Nonstandard Method

"GC/MS Determination of Volatile Halocarbons in Blood and Tissue" (Pellizzari, Sheldon, and Bursey 1985):

> This paper provides a method for detecting halocarbons including hexachloroethane in blood and tissue samples by using GC/MS techniques. The purge and trap method is used to extract the volatile halocarbons from samples and then thermally desorb them on to a GC/MS system. The limit of detection for 10 ml of blood is 3 ng/ml and 6 ng/g for 5-g tissue samples.

Development Trends

Abiotic Media

Analytical methods for detecting hexachloroethane in abiotic mediums such as soil, water, and air are listed in the previous section titled "Possible Methods." These standard methods have relied on solvent extraction of hexachloroethane followed by gas chromatography. Future development trends will likely focus on the minimization or elimination of solvents from sample preparation; methods such as Solid Phase Microextraction and/or thermal desorption may be tested. Gas chromatography is likely to remain the method of choice for determining this analyte.

Biotic Media

Some nonstandard analytical methods have been published for halocarbons in biological matrices including blood, urine, liver and fat tissues (Pellizzari, Sheldon, and Bursey 1985; Smith-Simon and Donohue 1994). The most suitable method for field screening of hexachloroethane in blood and tissue is listed in the previous section titled "Possible Methods." Most of these methods also rely on solvent extraction followed by GC analysis. There are ongoing studies in the development of analytical methods for hexachloroethane in blood by the Environmental Health Laboratory Sciences Division of the National Center for Environmental Health and Injury Control, Centers for Disease Control. These methods involve the purge and trap techniques followed by high-resolution gas chromatography and magnetic sector mass spectrometry (Bonin et al. 1992, Smith-Simon and Donohue 1994).

Recommended Methods

Standard Methods

For water or soil matrices, EPA Method 8121, which uses an electron-capture detector, will provide lower detection limits than EPA Method 8270C, which uses a mass spectrometer. However, since EPA Method 8270C is designed to detect a large suite of semi-volatiles, it may be the preferred method, depending on the objectives of the sampling effort. EPA Method 8270C is described in the chapter on anthraquinone. NIOSH Method 1003 is in unattached Appendix G of this report. Table 6-2 lists a brief summary of the recommended standard methods for hexachloroethane analysis.

Table 6-2. Recommended standard methods for hexachloroethane analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Solid	collect samples in glass container and store at 4°C	samples are solvent extracted in a Soxhlet or an Ultrasonic extractor	GC	ECD	1.1µg/kg of soil 16 µg/kg of sludge	$150 to $200
Aqueous	collect samples in glass container and store at 4°C	solvent extraction with organic solvent	GC	ECD	1.6 ng/L of water 0.016µg per Liter of waste-water	$150 to $200
Air	collect samples with solid sorbent tubes and tightly cap the samples before shipping	extract sorbent tubes with carbon disulfide	GC	FID	0.3 mg per m^3 for 70 liters of air	$100

* See Appendix A for a list of the standard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Nonstandard Method

The GC/MS method by Pellizzari, Sheldon, and Bursey (1985) for detecting halocarbons is recommended as a field screening method for detecting hexachloroethane in blood and tissue samples. This is a relatively a simple method that does not require any exhaustive extraction procedures. Table 6-3 lists a brief summary of the recommended nonstandard method for hexachloroethane.

Table 6-3. Recommended nonstandard method for hexachloroethane analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Blood and tissue	collect blood in vacutainer tubes, chill to 4°C and transfer to Teflon-lined screw-cap vial collect tissues and freeze immediately in a clean glass container with very little head space	analytes are extracted from samples via the purge and trap method and thermally desorbed prior to GC/MS analyses.	GC	MS	3 ng/ml for 10 ml of blood 6 ng/g for 5 g tissue	$400

* See Appendix B for a list of nonstandard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Procedures

Soil, Sludge, Water, and Wastewater Samples — EPA Method 8121

Sample Collection, Transport, and Storage QA/QC

Collect all samples in a wide-mouthed glass container with teflon-lined lid. Store samples at 4°C. Extract samples within 14 days of collection and analyze the extracts within 40 days of extraction. These guidelines are provided in unattached Appendix N of this report (Chapter Four - Organic Analytes, Section 4.1 - Sampling Considerations, from EPA SW-846 [EPA 1995b]).

Sample Preparation

EPA Methods 3510C and 3520C are recommended for sample preparation of aqueous samples. EPA Methods 3540C and 3550B are recommended for sample preparation of solid samples.

EPA Method 3500B — Organic Extraction and Sample Preparation:

This method provides guidelines and recommendations in reference to organic extractions and sample preparation procedures.

EPA Method 3510C — Separatory Funnel Liquid-Liquid Extraction:

This method involves extracting organic compounds from a water sample size of 1 Liter with 60 ml of methylene chloride at pH >11. Repeat this process

three times; collect and combine the extracts. Concentrate the extract using the Kuderna-Danish apparatus until a final volume of 1 ml is reached.

EPA Method 3520C —Continuous Liquid-Liquid Extraction:

This method involves extracting water-insoluble and slightly water-soluble organics from aqueous samples. The technique is similar to EPA Method 3510C except that the samples are extracted in a continuous liquid-liquid extractor. This procedure is used for samples containing emulsions or particulates (up to 1% solids).

EPA Method 3540C — Soxhlet Extraction:

Mix solid samples with sodium sulfate and place in an extraction thimble (or between two glass wool plugs). Extract samples with hexane:acetone (1:1) in a Soxhlet extractor. Dry and concentrate the resulting extracts with the K-D apparatus. Adjust the concentrated extract to a final volume of 10 ml with hexane.

EPA Method 3550B — Ultrasonic Extraction:

This method is used to extract nonvolatile and semivolatile compounds from soil, sludge, or waste samples by ultrasonic extraction with acetone:methylene chloride (1:1) solvent. Repeat the process three times and combine and filter the resulting extracts. Dry the extracts and concentrate them by using the K-D apparatus. This is a fairly rapid method but the extraction efficiency is not as good as other methods. However, this method does provide detailed procedures for sampling low and high concentrations of target analyte(s).

If cleanup procedures are necessary, EPA Methods 3620B and 3640A are recommended.

EPA Method 3620B — Florisil Cleanup:

Clean sample extracts by eluting the samples through florisil-packed GC columns or florisil-containing SPE cartridges. Florisil is a magnesium silicate with acidic properties. This process also separates out the target analyte(s) from the interfering compounds of different chemical polarity.

EPA Method 3640A — Gel Permeation Cleanup:

This method is recommended for eliminating lipids, polymers, copolymers, proteins, and natural resins from sample extracts. This method involves size exclusion cleanup with organic solvents and hydrophobic gels. A gel permeation cleanup column is packed with Bio Beads and flushed with methylene

chloride. After calibrating the column, sample extracts in methylene chloride are loaded onto the column.

Note: Quality control procedures for the extraction step are described in EPA Method 3500B, Organic Extraction and Sample Preparation. These procedures involve the use of surrogate standards (chemicals that are inert and not expected to be present in the environmental sample, the recoveries of which are used to monitor sample processing errors) that are added to each sample, blank, and matrix spike sample just before extraction. Recommended surrogate standards are 1,4-dichloronaphthalene, 2,6 trichlorotoluene, and 2,3,4,5,6-pentachlorotoluene. Matrix spike standards, blanks, and quality control check samples are also analyzed. For Method 8121, the quality control check samples contain hexachloro-substituted hydrocarbons at 10 mg/L in acetone.

Separation and Detection Parameters

1. Calibrate gas chromatograph as described in detail in EPA Method 8000B.
2. Inject 2-µL into the injection port of a gas chromatograph (65°C isothermal for column 1 or 75°C for column 2).
3. Analyze samples by gas chromatography. In addition, prepare and analyze blanks and quality control spikes.
4. Calculate and report analyte concentration (ng/L).
5. Quality control procedures for the performance of the gas chromatograph are described in *Test Methods for Evaluating Solid Waste,* 1995, SW-846 Method 8000B, Gas Chromatography. These involve analyzing calibration standards and calculating daily calibration factors that must vary by less than ±15% from the initial calibration.

Equipment and Chemical List

1. Equipment:
   a. Extractor (Soxhlet, Sonicator)
   b. Kuderna-Danish apparatus
   c. Gas chromatograph equipped with an Electron Capture Detector. GC Column 1 is a 30 m x 0.53 mm ID fused-silica capillary column bonded with trifluoropropyl methyl silicone; Column 2 is a 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with polyethylene glycol (PEG). (See method for dual column approach.) Gasses required for the analysis include 5% methane/95% argon.
   d. Assorted glassware (e.g., pipettes, vials, volumetric flasks, syringes, separatory funnels)
   e. Microsyringes and an analytical balance.

2. Reagents:
   a. Hexane, Acetone, Isooctane (2,2,4-trimethylpentane)
   b. Hexachloroethane (reference material).

Air Samples — NIOSH Method 1003

Sample Collection, Transport, and Storage QA/QC

1. Collect a designated volume of air with a calibrated sampling pump equipped with a glass solid sorbent tube containing two sections of 20/40 mesh activated coconut shell charcoal. Tubes are available commercially (SKC Inc., Eighty Four PA, 412-941-9701, Part. No. #226-01*). Guidelines for air sample collection are provided in unattached Appendix N of this report (Section D – General Considerations for Sampling Airborne Contaminants, from the *NIOSH Manual of Analytical Methods* [NIOSH 1994]).
2. Sample the air at a flow rate of 0.01 to 0.2 L/min for a minimum volume of 3 L and a maximum volume of 70 L.
3. Immediately after sampling, tightly cap samples and place in suitable containers for shipment to the lab as soon as possible. Label the samples with pertinent information including time of collection, temperature, humidity, and atmospheric pressure.

Sample Preparation

1. Prepare samples by placing the activated coconut shell charcoal-filled tube in a vial and adding carbon disulfide to desorb any hexachloroethane into the carbon disulfide.
2. Place sorbent tube in a vial with 1.0 ml of carbon disulfide and allow to stand 30 minutes with occasional agitation.
3. Determine desorption efficiency for each lot of charcoal tubes used for sampling. Spike sample tubes and blanks in triplicate at five levels using a small volume (2 to 20 µL) of the calibration stock solution. Age samples overnight, then desorb with solvent as real samples. In addition, analyze three quality control blind (i.e., prepared by someone other than the analyst) spikes and three analyst spikes.

Separation and Detection Parameters

1. Calibrate the gas chromatograph with at least six working standards in the range of 0.1 to 4 mg/ml.

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* Listing a company name does not constitute endorsement by the Federal government or the U.S. Army.

2. Analyze samples by gas chromatography. In addition, prepare and analyze blanks and quality control spikes.
3. Inject 5 µL of carbon disulfide extract into heated (170°C) injection port GC with column temperature of 110°C (isothermal).
4. Measure the peak area.
5. Calculate and report the concentration of the analyte (in mg/m^3).

Equipment and Chemical List

1. Equipment:
   a. Personal sampling pump with glass solid sorbent tube containing two sections of 20/40 mesh activated coconut shell charcoal.
   b. Gas chromatograph equipped with an FID. The GC column is a 3-m x 6-mm inner diameter (ID) glass packed with a 3% SP-2250, 80/100 mesh Chromosorb WHP. A DB-1 fused silica capillary column is listed as an alternative column. Gasses required for the analysis include hydrogen, air, and nitrogen.
   c. Assorted glassware (i.e., pipettes, vials, volumetric flasks, syringes).
2. Reagents:
   a. Hexachloroethane, reagent grade
   b. Hexachloroethane, 25 mg/ml in toluene
   c. Carbon disulfide, chromatographic quality
   d. Decane, n-undecane, or octane for internal standard.

Blood and Tissue Samples — Pellizzari, Sheldon, and Bursey (1985)

Sample Collection, Transport, and Storage QA/QC

1. Take 10-ml blood samples by brachial venipuncture using 10-ml vacutainer tubes. Use glass syringes instead of plastic syringes to prevent polymeric contamination. Chill collected samples to 4°C and place in Teflon-lined screw cap vials. Seal samples with teflon tape.
2. Collect 5-g tissue samples as close to as possible to postmortem. Place samples in a clean glass container with the least amount of headspace and freeze immediately.

Sample Preparation

1. Place a measured amount of blood (10 ml) into the purge flask and dilute with 50 ml purged, distilled, organic-free water. Place a stir bar in the flask and attach the flask to the 'purge/trap' apparatus. As the sample is stirring, raise the temperature to 50°C with the helium flow rate of 25 ml/min. After 90 minutes, stop the stirring and detach the Tenax cartridge from the purge apparatus and place it in a 5 ml Kimex culture tube containing Drierite. Cover the Kimex tube with glass wool, cap it, and place it in a freezer until analysis.

2. Place 10 g of tissue into the purge flask along with 50 ml of purged, distilled, organic-free water. While the flask is in an ice bath, macerate the tissue with a tissue homogenizer. Attach the flask to the purge apparatus and begin the stirring process, followed by a raise in temperature to 50°C with the helium flow of 25 ml/min. Stop the process in 30 minutes and store the Tenax cartridge in the Kimex tube as described above.

Separation and Detection Parameters

1. To ensure the proper functioning of the GC/MS system, analyze system performance standards to determine the sensitivity and performance of the system. Then calibrate the GC/MS system using standard solutions of the analyte of interest (250-450 ng). Analyze perfluorotoluene (150 ng) in conjunction with the standard solution, blanks, and samples to ensure proper quantification parameters. Set the GC/MS system with the following parameters:

Parameter	Setting
Inlet Manifold	
Desorption chamber & valve	270°C
Capillary trap - minimum	-195°C (cooled with nitrogen)
- maximum	240°C
Thermal desorption time	8 min
He purge flow	15 ml/min
GC	
60 m DB-1 wide-bore fused silica	40°C (hold 5 min), 240°C, 4°C/min
Carrier (He) flow	1.0 ml/min
Separator oven	240°C
MS	
scan range	m/z 35 to 350
scan cycle, automatic	1.9 s/cycle
filament current	0.5 mA
electron multiplier	1 600 volts
analyzer vacuum	18 mTorr
ion source vacuum	18 mTorr
inlet vacuum	25 mTorr
hold time	0.1 s

2. Place the Tenax cartridge containing the vapors from the system performance standards in the preheated desorption chamber and transfer the vapors to the capillary cold trap via helium.
3. Raise the temperature of the trap to 240°C at a rate of 100°C/min and pass the samples on to the GC column; analyze with the MS.
4. Repeat the above process with the calibration standards and determine the relative response factor.

5. Repeat the above process with blank cartridges followed by cartridges containing sample vapors from blood and tissue samples. Analyze the quantification standard, perfluorotoluene, with every cartridge.
6. Calculate and report concentrations of the analyte in µ/L for blood and in µg/kg for tissues.

Note: Instrument set-ups are provided in Pellizzari, Zweidinger, and Sheldon 1985b.

Equipment and Chemical List

1. Equipment:
   a. GC/MS system equipped with the following:
      - GC with fused silica capillary column connected to the ion source of the MS system.
      - MS with a low resolution quadrupole with the mass range of 1000 and the scan speed of 1 second to 10 minutes over the entire range and set in electron impact, chemical ionization mode.
      - inlet manifold that contains the desorption chamber, valve, and capillary trap interfaced with GC/MS system for thermal recovery of vapors from the Tenax tubes.
      - computer and plotter
   b. Glass cartridges (10 cm long x 1.5 cm ID)
   c. Soxhlet apparatus with condenser
   d. Vacuum oven
   e. Kimax tubes with teflon-lined screw-caps
   f. Vacutainer tubes
   g. Tissue homogenizer
   h. Tenax cartridges
   i. Purge apparatus
   j. Misc. items - glass wool, stainless steel mesh screens, magnetic stir bars, glass syringes, heating mantle, pipets, thermometer, and ice bath.
2. Reagents (all chemicals must be reagent grade):
   a. Distilled, organic-free water
   b. Compressed helium
   c. Drierite
   d. Calibration standards
   e. Hexachloroethane -pure analyte
   f. System performance standards
   g. Perfluorotoluene.

7 Terephthalic Acid

Use and Properties

Terephthalic acid and its analogs have been used in the production of linear crystalline polyester resins, films, and fibers due to their low volatility and high melting point (Moffitt et al. 1975, Sax and Lewis 1988). While terephthalic acid is not considered flammable, due to its physical form, electrostatic charges can build up during transport or storage (Fire Prevention Association 1991). Table 7-1 lists some common properties of terephthalic acid.

Table 7-1. Chemical and physical properties of terephthalic acid.

Chemical Name	Terephthalic Acid
Synonyms	1,4,-Benzenedicarboxylic Acid p-Carboxybenzoic acid p-Phthalic acid TPA
CAS Registry Number	100-21-0
Molecular Formula	$C_8H_6O_4$
Molecular Weight	166.13
Physical Description	white crystals or powder
Density	1.51g/ml
Melting Point	300^{o}C

Possible Methods

Standard Methods

No standard analytical method specific for terephthalic acid has been identified. However, an EPA Method for determining phthalate esters in aqueous and solid matrices has been identified.

In *Test Methods for Evaluating Solid Waste*, EPA SW-846 (EPA 1995b):

Method 8061A — This method uses GC/ECD (gas chromatography with electron capture detection) to determine the identities and concentrations of various

phthalate esters in aqueous and solid matrices including groundwater, leachate, soil, sludge, and sediment.

Nonstandard Methods

"Metabolism of terephthalic acid: Absorption of terephthalic acid from gastrointestinal tract and detection of its metabolites" (Hoshi and Kuretani 1967).

This paper focuses on determining the metabolism of terephthalic acid in rats. Rats are treated with radiolabeled terephthalic acid. Their gastrointestinal tracts are sampled and excretions are collected at various times after treatment. The authors use TLC to identify terephthalic acid and its metabolites.

"Absorption, distribution and excretion of terephthalic acid and dimethyl terephthalate" (Moffitt et al. 1975).

This paper describes a method similar to Hoshi and Kuretani (1967). Rats are orally dosed with radiolabeled terephthalic acid and tissue and fluid samples are taken at various times after treatment. This method assays for radioactivity to determine ^{14}C-labeled terephthalic acid.

"Reversed-phase high-performance liquid-chromatographic behavior of phthalic acid and terephthalic acid in the pH region around the second pK_a values" (Uno, Okumura, and Kawai 1994).

This paper describes a method for identifying terephthalic acid using reversed-phase HPLC techniques. This method, however, does not sample any environmental matrices or any biological fluids. Pure terephthalic acid is purchased commercially and recrystallized in ethanol prior to use.

"Anaerobic biodegradability of terephthalic acid and its inhibitory effect on anaerobic digestion" (Xin and Jusi 1994).

This paper describes the behavior of terephthalic acid in anaerobic conditions. Artificially created wastewater containing terephthalic acid is monitored for the ability to degrade terephthalic acid. Unfortunately, the UV photometer method for identifying terephthalic acid is not very well described in this paper. The authors do not provide any sample preparation steps or any limit of detection data.

Development Trends

Abiotic Media

The most currently cited method for detecting terephthalic acid in wastewater is listed above in the section on "Possible Methods."

Biotic Media

No current method for detecting terephthalic acid in biotic mediums was identified. Some older methods are listed in the section on "Possible Methods." However, these methods are not ideal for field screening and method development is needed for assaying terephthalic acid in biotic mediums.

Recommended Methods

Standard Method

EPA Method 8061A describes conditions for parallel column, dual electron, capture detection analysis of phthalate esters. The advantage of this method is that identification of compounds can be confirmed with another qualitative technique. However, this method does not specifically measure for terephthalic acid, so the retention time and minimum detection level should be established with a standard solution of terephthalic acid prior to sample analysis. Table 7-2 lists a brief summary of the recommended standard method for terephthalic acid analysis.

Table 7-2. Recommended standard method for terephthalic acid analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Aqueous sample	collect samples in glass container and store at 4°C	extract samples with SPE devices	GC	ECD	not provided	$320
Solid sample	collect samples in glass container and store at 4°C	extract with organic solvents in a Soxhlet extractor	GC	ECD	not provided	$350

* See Appendix A for a list of the standard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Nonstandard Method

The methods described above are not suitable for screening terephthalic acid in the field. The majority of these methods lack descriptive procedures that can readily be repeated. The method by Xin and Jusi (1994), which tests wastewater samples, would have been ideal for field screening but the method description is too vague. The detection of radiolabeled terephthalic acid is not realistic in field situations (Moffitt et al. 1975). The method by Uno, Okumura, and Kawai (1994) offers the most sensitive method for identifying terephthalic acid, but the authors do not provide sample preparation steps. The TLC method by Hoshi and Kuretani (1967) is recommended as a screening method for terephthalic acid in urine. The use of this method will not result in any quantitative data since radiolabeled terephthalic acid is not normally used in field situations; instead, the method will yield only the presence of terephthalic acid in test samples. This method is by no means an ideal screening method but due to difficulties in identifying a suitable method for terephthalic acid, the method by Hoshi and Kuretani (1967) is being recommended at this time. Table 7-3 lists a brief summary of this method.

Table 7-3. Recommended nonstandard method for terephthalic acid analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Urine	collect samples and fractionate into water, ethanol, and ether-soluble fractions	water-soluble fraction is neutralized to pH 7 and the ethanol- and ether-soluble fractions are acidified to pH 2. All fractions are concentrated	TLC	UV	not provided	$300

* See Appendix B for a list of the nonstandard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Procedures

Aqueous and Solid Samples — EPA Method 8061A

Sample Collection, Transport, and Storage QA/QC

Collect each sample in a wide-mouthed glass container with a teflon-lined lid. Store samples at 4°C. Extract samples within 14 days of collection and analyze the extracts within 40 days of extraction. These guidelines are provided in unat-

tached Appendix N of this report (Chapter Four - Organic Analytes, Section 4.1 - Sampling Considerations, from EPA SW-846 [EPA 1995b]).

Sample Preparation

The recommended sample preparation techniques for phthalate esters are EPA Method 3535 for aqueous samples and EPA Method 3540C for solid samples.

EPA Method 3535 — Solid-Phase Extraction

This method involves extracting target analyte(s) from aqueous samples by using SPE techniques. Elute analytes from the solid-phase medium with acetonitrile. Concentrate and dry the resulting extracts using the K-D concentration techniques. Adjust the concentrated extract to a final volume of 10 ml with hexane.

EPA Method 3540C — Soxhlet Extraction

Mix solid samples with sodium sulfate and place in an extraction thimble (or between two glass wool plugs). Extract the samples with hexane:acetone (1:1) in a Soxhlet extractor. Dry and concentrate the resulting extracts with the K-D techniques. Adjust the concentrated extract to a final volume of 10 ml with hexane.

If a cleanup procedure is necessary, EPA Methods 3610B and 3620B are recommended.

EPA Method 3610B — Alumina Cleanup

Clean sample extracts by eluting the samples through alumina-packed GC columns or alumina-containing SPE cartridges. This process separates out the target analyte(s) from the interfering compounds of different chemical polarity. The recovery of phthalate esters is slightly greater with this method compared to EPA Method 3620B.

EPA Method 3620B — Florisil Cleanup

Clean sample extracts by eluting the samples through florisil-packed GC columns or florisil-containing SPE cartridges. Florisil is a magnesium silicate with acidic properties. This process also separates out the target analyte(s) from the interfering compounds of different chemical polarity.

Separation and Detection Parameters

1. Set the gas chromatograph with the following operating conditions (for both columns 1 and 2):

Parameter	Setting
Carrier gas (He)	6 ml/min.
Makeup gas (N_2)	19 ml/min.
Injector temperature	250°C
Detector temperature	320°C
Injection volume	2 µl
Column temperature:	
Initial temperature	150°C, hold for 0.5 min
Temperature program	150°C to 220°C at 5°C/min followed by 220°C to 275°C at 3°C/min
Final temperature	275°C hold for 13 min

2. Calibrate the GC with calibration standards (at a minimum of five concentrations) and generate a standard curve for each of the analytes of interest. Calibration with an internal standard may also be done at this time. Detailed guidelines on calibration of GC are described in EPA Method 8000B (EPA 1995b).
3. Inject 2 µl of the sample into the injection port of the GC. Analyze blanks and quality control spikes.
4. Calculate and report analyte concentration (ng/L).
5. Quality control procedures for the performance of the GC are described in EPA Method 8000B (EPA 1995b). The procedures involve analyzing calibration standards and calculating daily calibration factors that must vary by less than ± 15% from the initial calibration.

Equipment and Chemical List

1. Equipment:
   a. Gas chromatograph with the capability for on-column and split/splitless injection and equipped with the following:
      - injection tee (8-in.) or glass Y splitter for megabore columns
      - column 1: 5% phenyl/95% methyl silicone fused-silica open tubular (DB-5, 30 m x 0.53 mm ID, 1.5 µm film thickness)
      - column 2: 14% cyanopropyl phenyl silicone fused-silica open tubular (DB-1701, 30 m x 0.53 mm ID, 1.0 µm film thickness)
      - detector: dual electron capture detector (ECD)
      - accessory materials including gases, syringes, recorder, and data system for measuring peaks heights or areas.
   b. Glassware including vials, flasks, beakers, graduated cylinders
   c. Kuderna-Danish apparatus
   d. Solid-phase extraction system including disks

e. Water bath, boil chips
f. Balance
g. Extractor (Soxhlet, Sonicator).

2. Reagents (all chemicals must be reagent grade):
   a. Hexane: pesticide quality or equivalent
   b. Methylene chloride
   c. Acetone
   d. Acetonitrile
   e. Sodium sulfate
   f. Organic-free reagent water
   g. Standard solutions:
      - stock standards
      - calibration standards: a minimum of five concentrations
      - internal standards: benzyl benzoate
      - surrogate standards: diphenyl phthalate, diphenyl isophthalate, and dibenzyl phthalate
      - matrix spike solutions: select phthalates of greatest interest.

Urine Samples — Hoshi and Kuretani (1967)

The method by Hoshi and Kuretani (1967) is a TLC method for identifying terephthalic acid and its metabolites in urine samples. (Only the TLC procedures are provided in this section.)

Sample Collection, Transport, and Storage QA/QC

Collect urine samples and fractionate into water, ethanol, and ether-soluble substances. Collect urine samples from control animals and fractionate in the same manner.

Sample Preparation

1. For water-soluble fraction in neutral pH: place 2 ml of urine in a test tube and adjust the pH to 7.0 by adding 1N NaOH. Concentrate the sample to 0.5 ml under vacuum in room temperature.
2. For ethanol-soluble fraction in acidic pH: place 2 ml of urine in a test tube and add 1N HCl until the pH of the urine reaches 2.0. Add 8 ml of ethanol and centrifuge. Evaporate the supernatant under vacuum at room temperature. Reconstitute the dried sample with 0.5 ml of ethanol.
3. For ether-soluble fraction in acidic pH: adjust 2 ml of urine to pH 2.0 with 1N HCl and 8 ml of ether. Transfer the ether layer to another test tube and evaporate it in the same manner as described above. Reconstitute the dried sample with 0.5 ml of ether.

Separation and Detection Parameters

1. Equilibrate TLC tanks with either solvent system I or solvent system II.
   Solvent system I (acidic) - n-butyl alcohol:acetone:water (60:20:20)
   Solvent system II (neutral) - n-butyl alcohol:ethanol (99.5%):water (80:20:20)
2. Spot 50- to 100-µl samples on the TLC plate along with pure terephthalic acid. Develop the plates in either solvent system I (acidic) or solvent system II (neutral).
3. Upon development, the resulting lines should overlap each other if the substances are identical. The R_f (retardation factor) value for terephthalic acid is 0.80. The UV-absorption is read at 254 mµ.

Equipment and Chemical List

1. Equipment:
   a. TLC apparatus:
      - silica gel GF_{254} mounted on glass plate (50 mm x 200 mm, 0.25 mm)
      - development tank
      - sample spotter
   b. Pipettes, beakers, flasks, test tubes
   c. UV detector.
2. Reagents:
   a. Sodium hydroxide (1N)
   b. Hydrochloric acid (1N)
   c. Ethanol
   d. Ether
   e. TLC solvents:
      - acidic solvent- *n*-BuOH:AcOH:H_2O (60:20:20)
      - neutral solvent- *n*-BuOH:99.5% EtOH:H_2O (80:20:20).

8 Titanium Dioxide

Use and Properties

Titanium dioxide is the major component of training smoke grenade, XM82 (Hilaski et al. 1991). It is also used by the military in conjunction with hexachloroethane in the production of white screening smoke (Karlsson et al. 1986). Titanium dioxide is a combustion product of titanium tetrachloride, which is also used as an obscurant (Department of Army 1963). Titanium dioxide is also used commercially in the production of white paint. Titanium dioxide is insoluble in water but there are no known reports of titanium dioxide persistence in the environment. The human population that has the highest potential of exposure would be workers in the titanium industry. Particulates of titanium dioxide have been identified in lung tissues of rats exposed to aerosols of titanium dioxide (Ferin et al. 1976). Table 8-1 lists some common properties of titanium dioxide.

Table 8-1. Chemical and physical properties of titanium dioxide.

Chemical Name	Titanium Dioxide
Synonyms	Titanium Oxide Titania Titanium White Brookite
CAS Registry Number	13463-67-7
Molecular Formula	O_2Ti
Molecular Weight	79.9
Physical Description	Translucent white-yellow solid
Density	4.17 g/ml
Melting Point	1835^oC

Possible Methods

Standard Methods

Standard methods for analyzing titanium dioxide in environmental matrices were not identified. However, there were standard methods for titanium metal.

In *Standard Methods for the Examination of Water and Wastewater* (APHA 1992):

Method 3111D — for the analysis of metals, including titanium, in water with AAS using the direct nitrous oxide-acetylene flame. This is the same method as EPA Method 283.1.

In *Methods for the Determination of Metals in Environmental Samples,* EPA-600/4-88/039, EPA-600/4-90/020 (Supplement 1), and EPA-600/R-92/129 (Supplement 2) (EPA 1991b):

Method 200.7 — for the analysis of metals, including titanium, in water, wastewater, and solid waste by ICP-AES.

Method 200.15 — for the analysis of metals, including titanium, in ground water and surface water by ultrasonic nebulization of ICP-AES.

In *Methods for Chemical Analysis of Water and Wastes,* EPA-600/4-79-020 (EPA 1983):

The majority of the metal methods in this manual are becoming obsolete due the similarity of methods in the APHA manual.

Methods 283.1 and 283.2 — both methods measure titanium in fresh and salt water and wastewater by AAS. Method 283.1 uses a direct aspiration technique while Method 283.2 offers a furnace technique.

In *NIOSH Manual of Analytical Methods* (NIOSH 1994):

Method 7300 — for the analysis of elements, including titanium, in air by using ICP-AES.

Method 8310 — for metal analysis (including titanium) in urine by using ICP-AES.

In *Official Methods of Analysis of AOAC International* (AOAC 1995):

Method 973.36 — a spectrophotometric method of detecting titanium in cheese.

Development Trends

Abiotic Media

No established analytical methods or ongoing studies in the development of analytical methods for titanium dioxide in water, soil, or sediments were identified. However, the general trend in analyzing titanium metal from environmental mediums mostly relies on two types of spectrometry: atomic absorption or atomic emission (Hilaski et al. 1991, Karlsson et al. 1986, EPA 1991b, APHA 1992, NIOSH 1994). The majority of these methods are listed in the previous section on "Possible Methods."

Biotic Media

The physical characteristics of titanium dioxide flakes were determined from lung tissues with the use of a scanning transmission electron microscope (STEM) or by electron probe x-ray microanalysis (ARL EMX-SM) and energy dispersive x-ray analysis (EDXA) (Ferin et al. 1976, Redline et al. 1986). No other analytical methods for detecting titanium dioxide in biotic mediums were identified.

Recommended Methods

The methods described in this section primarily use atomic absorption or atomic emission spectrometry to determine titanium metal in various matrices. The two NIOSH methods described in this section pertain to monitoring elements/metals to determine human exposure levels. However, both of these methods can be applied to field situations. NIOSH Method 7300 from the *NIOSH Manual of Analytical Methods* (NIOSH 1994) is recommended for the analysis of titanium in air and NIOSH Method 8310 for titanium in urine. EPA Method 200.7 from *Methods for the Determination of Metals in Environment Samples*, EPA-600/4-91/010 and EPA-600/R-94/111 (Supplement 1) (EPA 1991b) is recommended for determining titanium from water, wastewater, and solid waste samples. This method is similar to EPA method 200.15 except samples can have greater than 1% of undissolved solid. This method was chosen over other methods due to its versatility in analyzing water and solid samples. Table 8-2 lists a brief summary of the recommended standard methods for titanium dioxide analysis.

Procedures

Water, Wastewater, and Solid Waste Samples — EPA Method 200.7

Sample Collection, Transport, and Storage QA/QC

Aqueous Samples: For dissolved elements - filter the aqueous sample through a 0.45-µm pore diameter membrane filter at the time of collection. Acidify the filtrate with nitric acid to pH < 2 (use the (1:1) nitric acid concentration). Samples may be stored up to 6 months before analysis.

Table 8-2. Recommended standard methods for titanium dioxide analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Water and wastewater	dissolved elements- filter and acidify with nitric acid to pH < 2 total recoverable elements- acidify with nitric acid to pH < 2, hold for 16 hrs and verify pH	further acidify filtered sample with nitric acid further acidify sample with HNO_3 and HCl and heat	AES	ICP	1 µg/L	$50
Solid waste	collect sample & store at 4°C until analysis	sieve, acidify and heat sample	AES	ICP	0.2 mg/kg	$50
Air	after air sampling, filter holder is removed and tightly capped, then placed in a suitable container and shipped to the lab as soon as possible	acid digest	AES	ICP	1.2 ng/ml	$40
Urine	50 ml of urine is collected & preserved with 5 ml of HNO_3 in a PE bottle and shipped in refrigeration	filter through resin and acid digest	AES	ICP	0.1 µg per sample	$130

* See Appendix A for a list of the standard methods.

** Estimated total analysis cost, including sample preparation, per sample.

For total recoverable elements – acidify aqueous samples with nitric acid (1:1) to pH < 2. Mix samples and hold for 16 hours before checking the pH of the samples. This step verifies that the samples are maintaining an acidic pH. If the pH is > 2, add more acid.

Solid Samples: Collect solid samples and store at 4°C until analysis. There is no specified holding time.

Sample Preparation

1. Sample preparation for dissolved elements:
   Transfer more than 20 ml of the acidified filtrate into a 50-ml polypropylene centrifuge tube. Add a volume of nitric acid (1:1) that would be equivalent to 1% of the total volume. Cap and shake the tube. The sample is ready for analysis.

Note: The sample should be prepared as described in the procedure for total recoverable elements if precipitate forms during acidification, transport, or storage.

2. Sample preparation for total recoverable elements:
   Check the turbidity of the sample and make sure it is less than 1 NTU (nephelometric turbidity unit). Aliquot 100 ml of the sample into a 250-ml Griffin beaker and add 2 ml of nitric acid (1:1) and 1 ml of hydrochloric acid (1:1). Place the beaker on a hot plate (85°C) and evaporate the solution until the volume is approximately 20 ml. Take care not to boil the solution. Cool solution and transfer to a 50-ml flask. Centrifuge or leave the sample overnight to settle any undissolved material and analyze the clear portion.

Note: The sample preparation step for total recoverable elements is for all water samples except for drinking water. Drinking water can be prepared as described in the dissolved element preparation step (see the method for details).

3. Sample preparation for total recoverable analytes in solid samples:
   Mix sample and weigh out approximately 20 g and record weight. (If the moisture is greater than 35%, weigh out 50 to 100 g). Dry the samples to a constant weight at 60°C. Then sieve the sample using a 5-mesh polypropylene sieve and grind with the mortal and pestle. Weigh out 1 g of dried sieved sample and transfer to a 250-ml beaker for acid extraction. Add 4 ml of nitric acid (1:1) and 10 ml of HCl (1:4) to the beaker and cover with a watchglass. Heat the sample on a hot plate under a hood at 85°C for 30 minutes. Cool the sample and transfer to a 100-ml flask; bring to volume with water and mix. Centrifuge or leave the sample overnight to separate out the insoluble material. Analyze the clear extract.

Separation and Detection Parameters

1. Calibrate the atomic emission spectrometer according to the manufacturer's recommended procedures with the calibration standards and calibration blank. Set the wavelength at 334.9 nm for titanium. Prior to reading samples, establish the instrument performance and identify any spectral interference and correct for interference.
2. Analyze samples and standards. If the sample measurement is 90% or more of the upper limit of the linear dynamic range, dilute the sample until the analyte reading is within the linear dynamic range.
3. Calculate and report the concentration of analyte in m/L or mg/kg.
4. Quality control procedures consist of demonstrating instrument performance as well as laboratory performance. Establish a linear dynamic range and limit of detection and verify the calibration standards with quality control samples. Calibrate the instrument daily and analyze instrument performance check (IPC) solutions, laboratory reagent blanks, laboratory fortified blanks, as well as spectral interference check (SIC) solutions after every batch of 20 or fewer samples.

Equipment and Chemical List

1. Equipment:
   a. Inductively coupled plasma emission spectrometer equipped with:
      -background-correction capability (computer controlled)
      -argon gas supply
      -nebulizer with a peristaltic pump
   b. Analytical balance
   c. Hot plate, surface temperature 95°C
   d. Gravity convection drying oven maintained at 180°C
   e. Mortar and pestle
   f. Polypropylene sieve, 5 mesh (4-mm opening)
   g. Assorted labware: glass flasks, beakers, storage bottles, pipettes (refer to method for details).
2. Reagents (must be high purity reagents that meet the specifications of American Chemical Society):
   a. Hydrochloric Acid at various concentrations:
      -HCl - 1:1 (v:v) with water
      -HCl - 1:4 (v:v) with water
      -HCl - 1:20 (v:v) with water
   b. Nitric Acid at various concentrations:
      -HNO_3 - 1:1 (v:v) with water
      -HNO_3 - 1:2 (v:v) with water
      -HNO_3 - 1:5 (v:v) with water
      -HNO_3 - 1:9 (v:v) with water
   c. Reagent water

d. Ammonium hydroxide
e. Tartaric acid
f. Hydrogen peroxide: 50%
g. Standard stock solutions of titanium:
Dissolve 6.138 g $(NH_4)_2TiO(C_2O_4)_2$ H_2O in 100 ml reagent water. Dilute to volume in a 1-L volumetric flask with reagent water.
h. Calibration standard solutions:
Use a Ti-certified reference solution to make several Ti solutions of different concentrations.

i. Blanks:
-calibration blank
-laboratory reagent blank
-laboratory fortified blank
-rinse blank
j. Instrument Performance Check (IPC) solutions
2 mg/L method analyte in the same acid mixture as the calibration standards.
k. Quality Control Sample
Obtain this from an outside source different from the source of the standard stock solutions; it must be prepared in same acid mixture as the calibration standards.
l. Spectral Interference Check (SIC) solutions (refer to method for details).
m. Plasma solution.

Air Samples — NIOSH Method 7300

Sample Collection, Transport, and Storage QA/QC

1. Calibrate the sampling pump equipped with a cellulose ester membrane filter (0.8-µm pore size, 37-mm diameter, in cassette filter holder). Guidelines for air sample collection are provided in unattached Appendix N of this report (Section D - General Considerations for Sampling Airborne Contaminants, from the *NIOSH Manual of Analytical Methods* [NIOSH 1994]).
2. Sample the air at a flow rate of 1 to 4 L/min for a minimum volume of 5 L and a maximum volume of 100 L. Take two to four replicate samples.
3. Immediately after sampling, tightly cap the filter holder tubes and place in suitable containers for shipment to the lab as soon as possible. Label the filter holder tubes with pertinent information including time of collection, temperature, humidity, and atmospheric pressure.

Sample Preparation

1. Transfer the sample from the cassette filter holder to a clean beaker and add 5 ml of ashing acid. Cover with a watchglass and incubate at room temperature for 30 minutes. Heat the sample on a hotplate (120°C) to near dryness until the volume has been reduced to 0.5 ml. (Reagent blanks can also be started at this time).
2. Extract the sample multiple times with ashing acid (2 ml) and heat until the solution is clear. Perform all acid digestions under a well-ventilated hood.
3. Use water to rinse the beaker containing the sample and heat (150°C) to near dryness. Dissolve the residue with 2 to 3 ml of dilution acid. Transfer the sample to a 10-ml volumetric flask and dilute to volume with dilution acid.

Separation and Detection Parameters

1. Set and calibrate the spectrometer's conditions according to the manufacturer's recommendations and NIOSH guidelines. The wavelength for titanium is 334.9 nm. Also calibrate the unit with an acid blank and 10 µg/L of multi-element working solution in 4% HNO_3 and 1% $HClO_4$ containing titanium.
2. Analyze samples and standards. Dilute samples with dilution acid if the sample readings are above standard readings.
3. Calculate and report the concentration of the analyte (mg/m^3).
4. Analyze standards for every ten samples and check the recovery for two spiked media blanks per ten samples.

Equipment and Chemical List

1. Equipment:
   a. Personal sampling pump with a cellulose ester membrane (0.8-µm pore size, 37-mm diameter, in cassette filter holder).
   b. Spectrometer equipped with
      -inductively coupled plasma-atomic emission
      -two stage regulator
      -argon gas
   c. Hotplate, surface temperature 150°C
   d. Assorted glassware (i.e., beakers, watchglass covers, flasks) and pipettes.
2. Reagents:
   a. Acids - ultra pure and concentrated nitric acid and perchloric acid
   b. Ashing acid - HNO_3:$HClO_4$, 4:1 (v:v)
   c. Dilution acid - 4% HNO_3, 1% $HClO_4$ (add 50 ml of ashing acid to 600 ml of water, then dilute to final volume of 1 L)
   d. Calibration stock solutions - 1000 µg/ml of commercially prepared solution containing titanium.
   e. Distilled, deionized water.

Urine Samples — NIOSH Method 8310

Sample Collection, Transport, and Storage QA/QC

Collect 50 ml of urine and preserve with 5 ml of HNO_3 in a polyethylene bottle. Pack the sample in an insulated container and ship under refrigeration. Guidelines for collection of biological samples are provided in unattached Appendix N of this report (Section F - Special Considerations for Biological Samples, from the *NIOSH Manual of Analytical Methods* [NIOSH 1994]).

Sample Preparation

1. Extract the analytes from urine with polydithiocarbamate resin (60 mg) at pH 2.0 by shaking for 12 hours.
2. Filter the sample and re-extract the filtrate with more resin. Combine the collected resin and filter from the two extractions.
3. Perform an acid digest (similar to the one described in method 7300) on the collected resin and filter.
4. Dissolve the residue in 2 to 3 ml of dilution acid and dilute to a volume of 5 ml with deionized water.

Note: An aliquot of the urine sample is taken to determine the creatinine level.

Separation and Detection Parameters

1. Set and calibrate the spectrometer according to the manufacturer's recommendations. The wavelength for titanium is 334.9 nm. Also calibrate with an acid blank and 10 µg/L of multi-element working solution in 4% HNO_3 and 1% $HClO_4$ containing titanium.
2. Analyze standard and samples. If the sample readings are above the range of standards, dilute samples with 1 volume digestion acid plus 9 volumes of deionized water.
3. Calculate concentration of analyte (mg/m^3) but report results as µg of metal per g of creatinine.
4. Analyze standards after every ten samples and check recovery measurements with spiked urine samples (three) from unexposed people/animals after every ten samples.

Equipment and Chemical List

1. Equipment:
   a. Spectrometer equipped with
      -inductively coupled plasma-atomic emission
      -two stage regulator

-argon gas

b. Hotplate, surface temperature 100°C
c. Filtering apparatus for 50 ml liquid (47-mm cellulose ester, 0.8-µm pore size filters).
d. pH meter and electrodes
e. Mechanical shaker
f. Assorted glassware (i.e., beakers, watchglass covers, flasks) and pipettes. Polyethylene bottles - 125 or 250 ml. All labware must be washed with detergent, soaked 12 hours in 10% (v/v) HNO_3, and soaked 12 hours in deionized water.

2. Reagents:
   a. Polydithiocarbamate resin
   b. Acids - ultra pure and concentrated nitric acid and perchloric acid
   c. Dissolution acid or ashing acid - HNO_3:$HClO_4$, 4:1 (v:v)
   d. Dilution acid, 4% HNO_3, 1% $HClO_4$ (add 50 ml of ashing acid to 600 ml of water, then dilute to 1 L)
   e. Sodium hydroxide, 5 M (dissolve 20 g of NaOH in 50 ml boiled, deionized water; then dilute to 100 ml. Dilute again to a final volume of 1 L)
   f. Metal standards - 1000 µg/ml of commercially prepared solution containing titanium
   g. Distilled, deionized water.

9 Red Phosphorus

Use and Properites

Red phosphorus is used in the manufacture of phosphoric acid and other phosphorus compounds, and it is used in semiconductors, safety matches, and fireworks. When used as a smoke munition, red phosphorus is bound in a butyl rubber matrix, and is deployed using a tank-mounted self-protection grenade (Berkowitz et al. 1981). Table 9-1 lists some common properties of red phosphorus.

Table 9-1. Chemical and physical properties of red phosphorus.

Chemical Name	Red Phosphorus
Synonyms	RP RP/BR
CAS Registry Number	7723-14-0
Molecular Formula	P_n (polymeric)
Molecular Weight	
Physical Description	Violet-red amorphous powder
Density	2.16 to 2.31g/ml depending on form
Melting Point	585 to 600°C

Possible Methods

Standard Methods

No standard methods were identified for red phosphorus. Because red phosphorus is not soluble in water or in organic solvents, separation of red phosphorus from environmental matrices is difficult. However, when heated, red phosphorus will produce white phosphorus (P_4) vapor (Corbridge 1990). A NIOSH method for P_4 in air is described in Chapter 10, White Phosphorus.

Development Trends

Toxicity associated with red phosphorus has been attributed to the presence of white phosphorus as an impurity; pure red phosphorus is considered to have very low toxicity by ingestion (Berkowitz et al. 1981). Therefore, it is unlikely that analytical methods specifically for red phosphorus in environmental matrices will be developed.

Recommended Methods

Use those methods evaluated and recommended for white phosphorus (see Chapter 10).

10 White Phosphorus

Use and Properties

White phosphorus (P_4) has been used as a screening smoke by the U.S. military since World War I. Today it is used in a variety of projectiles including mortar rounds, howitzer rounds, rockets, and grenades. Also, white phosphorus is used commercially for the production of poisons, matches, and fireworks, and as a raw material to produce phosphoric acid (Parkes 1951). Environmental contamination with P_4 has occurred at facilities that either produce or use P_4 (Jangaard 1972, Pearson et al. 1976) and areas where P_4 munitions have been used (Racine et al. 1992, Racine et al. 1993). While unstable in aqueous solutions (Pourbaix 1966), P_4 residues persist in aquatic environments and have caused massive mortality of fish (Jangaard 1972) and waterfowl (Racine et al. 1992). Table 10-1 lists some common properties of white phosphorus.

Table 10-1. Chemical and physical properties of white phosphorus.

Chemical Name	White Phosphorus
Synonyms	Yellow Phosphorus WP WP/F Willie Peter
CAS Registry Number	007723-14-0
Molecular Formula	P4
Molecular Weight	124
Physical Description	solid waxy appearance smokes if exposed to air
Density	1.82 g/cm3
Melting Point	44°C

Possible Methods

Standard Methods

Two standard analytical methods for white phosphorus were located.

In *NIOSH Manual of Analytical Methods* (NIOSH 1994):
Method 7905 — for white phosphorus in air using a Tenax trap, solvent desorption, and gas chromatography.

In *Test Methods for Evaluating Solid Waste,* EPA SW-846 (EPA 1995b):
Method 7580 — this method determines P_4 in soil, sediment, and water by solvent extraction and GC analysis with a nitrogen-phosphorus detector (NPD). (This method was announced for public comment in the Federal Register on July 25; the comment period ended on September 25, 1995.)

Development Trends

Abiotic Media

Since the 1970s, gas chromatography with a phosphorus selective detector (either a nitrogen-phosphorus detector [NPD] or flame photometric detector [FPD]) has been used to analyze solvent extracts of samples containing white phosphorus. The NIOSH method relies on packed-column GC and will probably be updated to capillary-column GC. Future method development will likely focus on minimizing the use of organic solvents. For example, solid phase microextraction followed by thermal desorption in a gas chromatograph is being tested as a way to screen samples for white phosphorus contamination.

Biotic Media

White phosphorus has been assayed in fish and duck tissues by solvent extraction with an organic solvent followed by GC analysis equipped with an FPD or an NPD (Addison and Ackman 1970, Nam 1995, Racine et al. 1992, 1993). These methods are similar to analyses of abiotic samples but more studies are needed to establish them as standard methods.

Recommended Methods

Limits for white phosphorus in air and water have been set for the protection of health. Both standard methods provide detection capability below these limits. Table 10-2 lists a brief summary of the recommended standard methods for white phosphorus analysis.

NIOSH Method 7905 from *NIOSH Manual of Analytical Methods* (NIOSH 1994) is recommended for measuring white phosphorus concentration in air by using a GC with an FPD. The exposure limit for white phosphorus in air is 0.1 mg/m^3 according to NIOSH, Occupational Safety and Health Administration (OSHA), and ACGIH. Method 7905 is applicable over the range of 0.04 to 0.8 mg/m^3.

EPA Method 7580 from *Test Methods for Evaluating Solid Waste,* EPA SW-846 (EPA 1995b) is recommended for measuring white phosphorus in soil, sediment, and water samples using a GC-NPD. White phosphorus is extracted from samples with an organic solvent before analyses. The EPA has issued a Lifetime Health Advisory for white phosphorus in drinking water of 0.1 µg/L; criteria for the protection of aquatic organisms range from 0.01 to 0.04 µg/L. The method detection limit for Method 7580 is 0.008 µg/L.

Table 10-2. Recommended standard methods for white phosphorus analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Water	collect in pre-cleaned glass jar or bottle and store sample at 4°C in the dark	extract with organic solvent	GC	NPD	0.008 µg/L	$130
Soil/ sediment	collect in pre-cleaned glass jar or bottle and store sample at 4°C in the dark	extract with organic solvent	GC	NPD	0.4 µg/kg	$130
Air	collect sample with Tenax GC tubes and tightly cap the samples before shipping	extract with xylene	GC	FPD	0.04 mg per m^3 for 12 L air sample	$100

* See Appendix A for a list of the standard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Procedures

Water, Soil, and Sediment Samples — EPA Method 7580

Sample Collection, Transport, and Storage QA/QC

Collect a desired volume of soil, sediment, or water by completely filling a pre-cleaned glass jar or bottle. Immediately place the sample in the dark and chill to 4°C. The minimum sample volume should be 50 ml for soil or sediment and 1 L for water.

Sample Preparation

Extract a 40-g subsample of soil or sediment by 18 hours of vigorous shaking with 10 ml of isooctane and 10 or more ml of reagent grade water. Extract a 500-ml water sample with 50 ml of diethyl ether by shaking for 5 minutes; collect the ether phase. Reduce the volume of the ether phase by mixing it with approximately 50 ml of reagent grade water, then collect the remaining ether phase.

Separation and Detection Parameters

Prior to analysis of sample extracts, conduct a five-point calibration demonstrating linearity of the detector response with a zero intercept. Demonstrate acceptable accuracy and precision by analyzing four spiked samples of water and soil. Also analyze blanks, matrix spikes, and matrix spike duplicates for each batch of 20 samples.

1. Inject 1 µL of isooctane or ether extract into the injection port of the gas chromatograph with column temperature of 80°C (isothermal).
2. Measure peak area or peak height.
3. Calibrate the gas chromatograph with at least five working standards in the range of 3.5 to 72 µg/L.
4. Analyze samples by gas chromatography. In addition, prepare and analyze blanks and quality control spikes.
5. Calculate and report concentration of the analyte (µg/kg).

Equipment and Chemical List

1. Equipment:
   a. Platform shaker
   b. Vortex mixer
   c. Gas chromatograph equipped with a NPD. The GC column is a 15-m, wide-bore (0.53 mm) capillary column, 100% methyl silicone, 3.0 µm film thickness. Gasses required for the analysis include nitrogen, hydrogen, and air.

d. Analytical balance
e. Assorted glassware (i.e., pipettes, vials, volumetric flasks, syringes, separatory funnels)

2. Reagents:
   a. Phosphorus (white), stored under distilled water
   b. Isooctane (2,2,4-trimethylpentane)
   c. Diethyl ether, pesticide grade
   d. Water, reagent grade.

Air Samples — NIOSH Method 7905

Sample Collection, Transport, and Storage QA/QC

1. Calibrate the sampling pump equipped with a glass solid-sorbent tube containing Tenax. Various manufacturers provide tubes specifically designed for Method 7905. Some examples include SKC Inc, (Eighty Four, PA, 412-941-9701, Part. No.#226-35-03) and Supelco, Inc. (Supelco Park, PA, 800-247-6628, Part Number 2-0832). Guidelines for air sample collection are provided in unattached Appendix N of this report (Section D - General Considerations for Sampling Airborne Contaminants, from the *NIOSH Manual of Analytical Methods* [NIOSH 1994]).
2. Collect a minimum volume of 5 L and a maximum volume of 100 L of air with the calibrated sampling pump at a flow rate of 0.01 to 0.1 L/minute.
3. Immediately after sampling, tightly cap samples and place in suitable containers for shipment to the lab as soon as possible. Label the samples with pertinent information including time of collection, temperature, humidity, and atmospheric pressure.

Sample Preparation

1. Place sorbent tube in a vial with 1.0 ml of xylene and allow it to stand 30 minutes with occasional agitation.
2. Determine desorption efficiency for each batch of Tenax tubes used for sampling. Spike sample tubes and blanks in triplicate at five levels using a small volume (2 to 20 µL) of the calibration stock solution. Age samples overnight, then desorb with solvent as real samples. In addition, analyze three quality control blind (i.e., prepared by someone other than the analyst) spikes and three analyst spikes.

Separation and Detection Parameters

1. Analyze samples by gas chromatography. In addition, prepare and analyze blanks and quality control spikes.
2. Calibrate the gas chromatograph with at least six working standards in the range of 0.01 to 5 µg/ml.

3. Inject 5 µL of xylene extract into a heated (200°C) injection port GC with column temperature of 80°C (isothermal).
4. Measure peak area. Calculate and report the concentration of the analyte (in mg/m^3).

Equipment and Chemical List

1. Equipment:
   a. Personal sampling pump with Tenax-filled tube. If air sample potentially contains particulate white phosphorus, a cellulose ester membrane filter is added to the Tenax tube.
   b. Gas chromatograph equipped with an FPD. The GC column is a 1.8-m x 6-mm ID glass packed with a 3% OV- 101,80/100 mesh Chromosorb WHP. Gasses required for the analysis include helium, hydrogen, air, and nitrogen.
   c. Analytical balance
   d. Assorted glassware (i.e., pipettes, vials, volumetric flasks, syringes).
2. Reagents:
   a. Phosphorus (white), stored under distilled water
   b. Xylene (mixed), reagent grade
   c. Acetone.

11 Polyethylene Glycol

Use and Properties

Polyethylene glycol (PEG) is a dihdroxy derivative of a paraffin. The formula weight of PEG ranges from 200 to 10,000. It is used for industrial applications such as lubricants, plasticizers, and binders, and pharmaceutical applications such as components of water-based ointments, drugs, and cosmetics (Crook et al. 1981, Muhly 1983). PEG 200, the smallest member of the PEG family, is used by the military as a smoke obscurant (Crook et al. 1981, Muhly 1983). The smoke generated by PEG 200 is very similar to fog oil smoke, but is less toxic (Muhly 1983). Consequently, the Army investigated PEG 200 as a possible replacement for fog oil and diesel fuel as a smoke obscurant (Crook et al. 1981, Muhly 1983). Table 11-1 lists some common properties of PEG.

Table 11-1. Chemical and physical properties of polyethylene glycol.

Chemical Name	Polyethylene Glycol
Synonyms	PEG
CAS Registry Number	25322-68-3
Molecular Formula	$C_8H_{18}O_5$
Molecular Weight	200-10,000 (The molecular weight range of PEG that is used for military obscurant is 190-210.)
Physical Description	water-white liquid
Density	1.125 g/cm (25^oC)
Melting Point	

Possible Methods

Standard Methods

No standard analytical method for PEG 200 was identified. However, an EPA method for determining PEG 600 in aqueous samples was identified.

In *Analytical Methods for the Determination of Pollutants in Pharmaceutical Manufacturing Industry Wastewater* (EPA 1995):
Method 1673 — HPLC method for determining PEG 600 from wastewater.

Nonstandard Methods

"High-performance liquid chromatographic method for the simultaneous determination of low-molecular-mass oligomers of polyethylene glycol in aqueous skin extracts" (Ruddy and Hadzija 1994):

> This method uses the isocratic reversed-phase HPLC technique to determine low molecular PEGs (molecular weights ranging from 200 to 1000) in rat skin extracts. Samples are isolated and purified by SPE prior to analyses. This method is advantageous in that low molecular mass oligomers of PEG can be identified simultaneously without any additional size separation processes before analyses and the error involved in the recovery of individual polymers is approximately 3%. However, the recovery of PEGs with molecular weights lower than 282 is approximately 18.28%, while the limit of detection for PEG 200 is 100 µg/ml.

"Separation and quantitation of polyethylene glycols 400 and 3350 for human urine by high-performance-liquid chromatography (Ryan, Yarmush, and Tompkins 1992):

> The method described in this paper separates and identifies PEG 400 and 3350 in human urine. Samples are prepared by filtering through sized regenerated cellulose membranes and mixed ion-exchange resins, and quantified by refractive indices via HPLC. The limit of detection is approximately 0.005 mg/ml for PEG 3350 and 0.05 mg/ml for PEG 400. The advantages of this method include the elimination of liquid-liquid extraction or radiolabeling of compounds.

"New extraction procedure and high-performance liquid chromatographic method for analyzing polyethylene glycol-400 in urine" (Schwertner et al. 1992):

> This paper describes a new method for identifying PEG 400 in human urine by using isocratic reversed-phase HPLC. The samples are extracted with a salt-solvent combination of ammonium sulfate and dichloromethane. This process does away with the need to filter samples through ion-exchange resin and also the need to separate individual polymers before analysis. However, the detection limit for this method is not quite as sensitive as the previous method by Ryan, Yarmush, and Tompkins (1992). The limit of detection was approximately 0.25 g/L for a 2-ml urine sample.

Development Trends

Abiotic Media

The most current methods for detecting PEG include GC/FT-IR with supercritical fluid extraction (Gurka et al. 1994) and HPLC with evaporative light scattering detection (Rissler, Fuchslueger, and Grether 1994). Both of these methods describe the actual techniques and procedures for detecting the pure compound rather than sampling any environmental matrices.

Biotic Media

There are many nonstandard methods for determining PEG (in the molecular weight range of 400 to 3350) from skin extracts and biological fluids such as urine by using HPLC methods (Kwong, Baert, and Bechard 1995; Ruddy and Hadzija 1994; Ryan, Yarmush, and Tompkins 1992; Schwertner et al. 1992). These methods are listed in the previous section on "Possible Methods."

Recommended Methods

Standard Method

EPA Method 1673 from *Analytical Methods for the Determination of Pollutants in Pharmaceutical Manufacturing Industry Wastewater* (EPA 1995) is recommended for detecting PEG 200 in wastewater. This method is designed to determine PEG 600 in wastewater, but the separation and detection parameters may also be used to detect PEG 200. The retention time and calibration curve for PEG 200 needs to be generated prior to any wastewater sampling. Table 11-2 lists a brief summary of the recommended standard method for PEG analysis.

Table 11-2. Recommended standard method for PEG analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Waste-water	collect in glass con-tainer and store sample at 0-4°C	extract with dichloro-methane & K-D ap-paratus. then de-rivatize with 3,5dinitro-benzoyl chloride	HPLC	UV	1 mg/L	$400

* See Appendix A for a list of the standard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Nonstandard Method

The three current methods listed in the previous section all use HPLC techniques to determine PEG in human urine or in skin extracts. All three methods have the capability of being used to test animal fluids. However, the method by Schwertner et al. (1992) is recommended for use as the field screening method. This method is relatively simple and less time consuming in that the samples can be collected and frozen until use. Also, the extraction procedures are less labor intensive than other methods. The sensitivity of this method is not as high as the other methods, but the toxicity due to PEG is low and detection levels in microgram quantities are not necessary. The method by Ruddy and Hadzija (1994) does screen for PEG 200 in skin extracts but the recovery efficiency of PEG 200 from the sample medium is low, approximately 18%. Table 11-3 lists a brief summary of the recommended nonstandard method of PEG analysis.

Table 11-3. Recommended nonstandard method for PEG analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Urine	collect in glass container and store sample at -20°C	salt-solvent extraction	HPLC	UV	0.25 g/L for 2 ml urine	$300

* See Appendix B for a list of the nonstandard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Procedures

Wastewater Samples — EPA Method 1673

Sample Collection, Transport, and Storage QA/QC

Collect wastewater samples in a glass container (>1 L) and seal (with no air bubbles) until analysis. Store the samples at 0 to 4°C until analysis. Extract samples within 5 days of collection, derivatize within 7 days of extraction, and analyze within 4 days of derivatization.

Sample Preparation

1. Extract 1 liter of the sample in a liquid-liquid extractor with dichloromethane for 18 hours along with 1 ml of surrogate standards or 1 L of calibration standard.
2. Using K-D procedures, evaporate the solvent, dichloromethane, by pouring the sample over anhydrous sodium sulfate. Further evaporate the solvent with a gentle stream of nitrogen until the sample volume is approximately 10 to 25 ml.

Transfer the residue to a vial with V-shaped chamber using anhydrous dichloromethane or anhydrous tetrahydrofuran.

3. Derivatize a water-free sample with 5 ml of 3,5-dinitrobenzoyl chloride in anhydrous tetrahydrofuran (10 mg/ml) and two drops of anhydrous pyridine. Heat the sample in a sand bath for 1 hr at 60°C.
4. Cool the sample and transfer to a 125-ml separatory funnel, adding 50 ml of diethyl ether. Being careful not to loose any ether, sequentially extract the sample with two 25-ml portions of dilute HCl, two 25-ml portions of reagent water, two 25-ml portions of sodium bicarbonate solution, and two 25-ml portions of saturated sodium chloride solution.
5. Filter the sample through glass wool containing 10 g of anhydrous sodium sulfate. Transfer the filtrate to a K-D apparatus and evaporate most of the solvent.
6. Perform solvent exchange with 40% acetonitrile in water. Adjust the volume to 2 ml and filter the sample, if necessary, before analysis.

Separation and Detection Parameters

1. Calibrate and set the desired conditions for the HPLC. Set the UV detector at 254 nm and an injection volume of 50 µl. The retention time for PEG 600 is approximately 0.63 minutes. Create a linear calibration curve.
2. Analyze samples and standards and record the peak area. If the response is not within the linear range of the calibration curve, inject a smaller volume or dilute with 40% acetonitrile/water.
3. Calculate the response factor and report the concentration in mg/ml.
4. Conduct quality control by establishing a laboratory demonstration of acceptable precision and accuracy by analyzing 4 aliquots of performance standards and determining the average recovery of analyte and the standard deviation. Analyze blanks containing reagent water throughout the extraction and derivatization process to show that blanks are indeed free of any contamination. However, if a blank measures greater than 200 µg/L of PEG 600, stop the process until the source of contamination is negated. Calibrate the instrument with calibration standards and verify with external calibration standards. Analyze spiked samples to determine the accuracy of the analysis.

Equipment and Chemical List

1. Equipment:
   a. High-performance liquid chromatograph equipped with:
      -pumping system - 2 ml/min
      -high-pressure injection valve or autosampler
      -column – 25-mm x 4.6-mm ID, 5 µm, Betasil C_{18}
      -absorbance detector - 254 nm
      -strip chart recorder compatible with detector

b. Kuderna-Danish (K-D) apparatus with
   -10 ml graduated concentrator tubes with ground-glass stoppers
   -500-ml evaporation flask
   -two micro and three macro Ball Synder Columns
   -half-inch springs
c. Liquid-liquid extractor (1 L)
d. Reaction vessel (5-ml screw-cap vial with V-shaped chamber)
e. Analytical balance (weighing to nearest 0.1 mg)
f. Boiling chips and glass-fiber paper (0.6 to 0.9 µm)
g. Water bath and sand bath
h. Microsyringes – 10 and 100 µl
i. Assorted glassware: flasks, vials, bottles, pipettes.

2. Reagents (all chemicals must be reagent or pesticide grade):
   a. Reagent water
   b. Dichloromethane
   c. Acetonitrile
   d. Diethyl ether
   e. Tetrahydrofuran, anhydrous
   f. Surrogate- Di(ethylene glycol) monohexyl ether
   g. Sodium sulfate, anhydrous
   h. Hydrochloric acid solution (100 ml to approximately 1 L of water)
   i. Sodium bicarbonate solution (10 g to approximately 1 L of water)
   j. Saturated sodium chloride solution
   k. Pyridine, anhydrous
   l. 3,5-Dinitrobenzoyl chloride in anhydrous tetrahydrofuran (10 mg/ml)
   m. Stock standard solutions
      -stock PEG-600
      -secondary standard
      -surrogate standard
      -performance standard.

Urine Samples — Schwertner et al. (1992)

Sample Collection, Transport, and Storage QA/QC

Collect urine samples 6 hours after the subject consumed the PEG 400. Measure the volume of the urine and store at -20°C until testing.

Sample Preparation

1. Add approximately 2.5 g of ammonium sulfate to a 125- x 16-mm glass screw-capped tube containing 2 ml of urine. Mix the sample thoroughly for 20 seconds on a vortex shaker.
2. Add 10 ml of dichloromethane and shake for 15 minutes on an Eberbach shaker.

3. Spin the samples for 10 minutes at 2000g and at 25°C. Transfer 8 ml of the dichloromethane phase to a scintillation vial and evaporate at 50°C under nitrogen or air.
4. Resuspend the sample with 2 ml of methanol:water mobile phase; it is ready for analysis.

Separation and Detection Parameters

1. Calibrate the HPLC system and generate a standard curve with PEG concentrations ranging from 2.5 to 10 g/L.
2. Inject 200 µl of the sample into the HPLC. Determine the concentration of PEG (g/L) by comparing the peak areas of the sample to those of the standard PEG.
3. Determine the recovery efficiency by extracting PEG-spiked urine samples using the same method described above. The extraction efficiency is approximately 96 to 97%. Generate a standard curve that is linear up to PEG concentration of 10 g/L. Within- and between-day assay coefficients of variations should be less than 5% in 10 samples.

Equipment and Chemical List

1. Equipment:
   a. HPLC equipped with the following system and conditions:
      - 600E system controller
      - 410 differential refractometer, operated at 40°C
      - µBondapak C_{18} reversed-phase column, 30 cm x 3.9 mm ID, particle size 10 µm
      - flow rate of 1 ml/min at ambient temperature
      - injection volume of 200 µl
      - mobile phase of methanol:water (50:50, v:v) [use methanol:water (30:70, v:v) for PEG 200 (Ruddy and Hadzija 1994)
   b. Glass screw-capped tubes (125 x 16 mm)
   c. Eberbach shaker and vortex shaker
   d. Centrifuge
   e. Miscellaneous glassware (i.e., disposable glass tubes, volumetric pipettes, Pasteur pipettes, scintillation vials)
   f. Funnels and spatula.
2. Reagents:
   a. Dichloromethane
   b. Ammonium sulfate
   c. PEG 400, 600, 1000
   d. Water
   e. Calibration standards of PEG (2.5, 5.0, and 10.0 g/L in methanol:water, 50:50)
   f. Urine-based standards of PEG (2.5 and 5.0 g/L in fresh collected urine).

12 (o-Chlorobenzal)malononitrile

Use and Properties

(o-Chlorobenzal)malononitrile, also known as CS, has been one of the most widely used riot-control agents since 1958 (Keller, Elves, and Bonnin 1986). CS is a potent lacrimator and irritates the eyes, nose, mouth, and the respiratory tract. It is used by law enforcement agencies to control public disturbances and by the military in terrain denial and in training. CS has a lower incapacitating threshold compared to other riot-controlling agents; the onset of action is fairly rapid after exposure. CS has been found to persist in snow for as long as 30 days but its persistency in soil varied, depending on the condition of the soil (Keller, Elves, and Bonnin 1986). Table 12-1 lists some common properties of CS.

Table 12-1. Chemical and physical properties of (o-Chlorobenzal)malononitrile.

Chemical Name	Propanedinitrile [(2-chlorophenyl)methylene]-
Synonyms	2-chlorobenzalmalononitrile (o-chlorobenzylidene)malononitrile CS o-Chlorobenzylidenemalonic nitrile
CAS Registry Number	2698-41-1
Molecular Formula	$C_{10}H_5ClN_2$
Molecular Weight	188.03
Physical Description	White crystalline solid with odor of pepper
Density	
Melting Point	

Possible Methods

Standard Methods

No standard analytical method for CS has been identified.

Nonstandard Methods

"Environmental effects of fog oil and CS usage at the combat maneuver training center, Hohenfels, Germany" (Brubaker, Rosenblatt, and Synder 1992):

This report provides a method for detecting CS and a metabolite of CS in soil and plant samples using a capillary GC equipped with an FID. The authors provide very detailed procedures for sampling, sample preparation, and analysis. Samples are extracted by a salt-solvent combination of sodium sulfate and methylene chloride-acetone or hexane-acetone. The limit of detection is approximately 19 ppm of CS in 30 g of soil.

"Behavior of chemical agents in seawater" (Demek et al. 1970):

This report provides brief GC-FID and spectrophotometer procedures for measuring CS in seawater that has been spiked with CS. The main objective of this report was to provide information on the behavior of chemical agents including CS in seawater; therefore, the descriptions of the analytical methods are very brief and not very detailed.

"Concise identification of commonly encountered tear gases" (Gag and Merck 1977):

This paper briefly describes an IR spectrometry method for detecting CS from a tear-gas aerosol canister called Paralyzer Model X621. CS is extracted from the oily carrier with ethanol and hexane. The crystals of CS are identified by IR spectrometry.

"Methods for analysis of contaminated soil in Pine Bluff Arsenal, Pine Bluff, Arkansas" (Gosnell 1976):

This report provides a method for extracting and analyzing organic compounds including CS from soil samples. Samples are extracted with sodium sulfate and hexane-acetone mixture (50:50, v:v) and identified by packed-column GC with an electron capture detector.

"Analysis of snow samples contaminated with chemical warfare agents" (Johnsen and Blanch 1984):

This paper describes results obtained from the analyses of snow samples for chemical warfare agents, including CS. To simulate field conditions, chemical warfare agents are aerosolized onto the surfaces of snow and analyzed at various times after treatment. Samples are extracted immediately after collection with chloroform or trioctylamine in chloroform. The authors state that the samples are then analyzed by GC, MS, or HPLC, but do not provide any set-up conditions for these instruments.

"Analytical methods development and analysis of Camp Simms soil samples for o-chlorobenzylidenemalononitrile and o-chlorobenzaldehyde" (Jones and Grady 1981):

> This report describes a method for identifying CS and metabolites of CS in soil samples by using HPLC procedures. Samples are solvent-extracted with methylene chloride before analyses. The sensitivity of this assay is approximately 1.25 ppm of CS with the limit of detection being 1.7 ppm of CS in a 50-g soil sample.

"Identification of chemical warfare agents in air samples using capillary column gas chromatography with three simultaneous detectors" (Kaipainen, Kostiainen, and Riekkola 1992):

> This paper describes methods for detecting chemical warfare agents, including CS, in air samples by using a capillary-column GC equipped with FID, PID, and TID. Absorbent tubes that are used in the collection of air samples are spiked with chemical warfare agents before air collection. Samples are thermally desorbed rather than solvent desorbed and analytes are identified by their retention indices.

"Assessment of CS environmental toxicity at Eglin AFB FL" (Keller, Elves, and Bonnin 1986):

> This report provides a liquid chromatography (LC) method for identifying CS in soil. Soil samples are sprayed with 1% CS and incubated at various conditions to simulate field conditions. Samples are extracted in methylene chloride and identified with UV detection.

"A comparison of ionization techniques for gas chromatography/mass spectroscopy analysis of dye and lachrymator residues from exploding bank security devices" (Martz, Reutter, and Lasswell 1983):

> This paper describes GC/MS techniques in comparing the effectiveness of three types of detectors for detecting CS. CS is identified with the following detectors: (1) negative ion chemical ionization (NICI), (2) electron impact ionization (EI), and (3) positive ion chemical ionization (PICI). This method does not sample CS from any environmental matrices but rather uses commercially available CS. The NICI detector was more effective in detecting lower levels of CS compared to the other two detectors.

"TLC analysis of warfare agents under battlefield conditions" (Sokolowski and Rozylo 1993):

> This paper describes TLC techniques for detecting chemical warfare agents including CS. The authors state that their method can be used to identify chemical warfare agents from various environmental matrices including wa-

ter, soil, vegetation, and foodstuff, but do not provide any sampling or sample preparation procedures. If sample preparation methods are provided, this method may be useful in rapidly determining chemical warfare agent contamination without any quantitative analysis.

Development Trends

Abiotic Media

For the past 10 years CS has been identified in various abiotic mediums by several different detection techniques. CS has been identified by IR spectroscopy, GC/MS in chemical ionization mode, GC, LC, and HPLC in mediums such as snow and soil. Most of these methods are listed in the previous section titled "Possible Methods." The current trend in analyzing CS involves the use of instruments such as HPLC, GC, GC/MS, and high-resolution gas chromatography-retention index monitoring (HRGC-RIM) (Kokko 1993; Kaipainen, Kostiainen, and Riekkola 1992). TLC techniques are also being used to rapidly detect contamination of CS and other types of chemical warfare agents (Sokolowski and Rozylo 1993).

Biotic Media

Analytical methods for detecting CS in biological mediums such as animal tissues, blood, or urine, were not identified. Numerous in vivo and in vitro toxicological studies on the effects of CS were identified. The majority of these studies did not provide analysis methods for measuring CS in their respective mediums; rather, they provided procedures in determining toxicity (Ballantyne and Swanston 1978; Meshram, Malini, and Rao 1992; Weller, Kubbies, and Nusse (1995). The analysis method by Brubaker, Rosenblatt, and Synder (1992) was the only method that provided procedures for assaying CS in plant samples. This method is listed in the previous section titled "Possible Methods."

Recommended Methods

Nonstandard Methods

All methods listed above specifically assay for CS or include CS as one of the analytes being monitored, but only a few are useful as a field screening method. Methods by Gag and Merck (1977), Johnsen and Blanch (1984), Martz, Reutter, and Lasswell (1983), and Sokolowski and Rozylo (1993) all lacked detailed proce-

dures on sample preparation, instrument set-up, or both. Methods by Keller, Elves, and Bonnin (1986); Gosnell (1976); and Brubaker, Rosenblatt, and Synder (1992), while providing very descriptive sampling and analytical procedures, are less sensitive than the method by Jones and Grady (1981). Jones and Grady (1981) provide procedures for the analysis of CS in soil; their method may also be modified to analyze vegetation samples. One disadvantage in the method by Jones and Grady (1981) is that they do not provide adequate information on sample collection. Sample collection methods by Brubaker, Rosenblatt, and Synder (1992) can be substituted in place due to the fact that the methods are very similar to standard sample collection procedures. Demek et al. (1970) provides the only method for detecting CS in seawater; this method cannot be recommended due to use of outdated techniques and insufficient information on detection parameters. The method by Kaipainen, Kostiainen, and Riekkola (1992) is recommended for CS detection in air. This method may be quite useful in field situations since the analytes are thermally desorbed from the adsorbent tubes rather than solvent extracted. Table 12-2 lists a brief summary of the recommended nonstandard methods for CS analysis.

Table 12-2. Recommended nonstandard methods for CS analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Soil	collect soil samples and mix until homogeneous, then transfer to clean 250 ml sample bottle	Soxhlet solvent extraction followed by K-D concentration	HPLC	UV	1.7 ppm for 50g soil	$450
Air	collect 20 dm^3 of air approximately 5 to 10 cm above ground	sampling tubes thermally desorbed	GC	FID PID TID	not provided	$340

* See Appendix B for a list of the nonstandard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Procedures

Soil Samples — Jones and Grady (1981)

Sample Collection, Transport, and Storage QA/QC

1. Mark the center of the sampling location with a square that is approximately 10 m each side.

2. Locate another square that is approximately 8 cm each side and pull it free of any vegetation before soil collection.
3. Using a precleaned stainless steel spoon, take soil samples from the 8-cm square area to a depth of 4 cm. Place the collected samples in a stainless steel tray lined with aluminum foil and mix thoroughly.
4. Place the homogeneously mixed soil samples into a precleaned, 250-ml glass sample bottle until it is full. Discard the remaining samples.
5. Wipe the sample bottles clean of debris and label them.
6. Take five grab samples and duplicates from one location.

Note: Guidelines for soil sample collection are found in unattached Appendix E of this report (Brubaker, Rosenblatt, and Synder 1992).

Sample Preparation

1. Place a 50-g soil sample in the Soxhlet extraction apparatus with 200 ml of methylene chloride. Cover the extraction thimble with glass wool to prevent sample loss. Add methylene chloride to the flat-bottomed reflux flask. Place the condenser hose securely and check the water for adequate flow. Extract the sample(s) overnight (or 6 to 8 hours).
2. Dry the soil extract by passing it through 20 g of sodium sulfate. Place the clean sodium sulfate in a 250-ml separatory funnel with a glass wool plug and a Teflon stopcock. Slowly pour the sample extract into the separatory funnel and collect the dried extract dropwise until the entire sample has eluted. Rinse the sodium sulfate three times with small amounts of methylene chloride; add the wash to the dried sample.
3. Concentrate the extract in a Kuderna-Danish apparatus by steam to a final volume of 2 ml. Transfer the extract to a 10-ml volumetric flask and bring to a final volume of 10 ml with hexane. This sample will resemble the 20% methylene chloride in hexane being used as the mobile phase.

Separation and Detection Parameters

1. Analyze the extracts by reverse-phase HPLC using a Bondapak CN column and UV detection at 260 nm. The retention time for CS is 310 seconds (approximately 5 minutes) and for CEA it is 235 seconds (approximately 4 minutes).
2. Prepare calibration standards and generate standard curves by plotting concentration (mg/ml) vs peak area. Determine the sample concentration by correlating the sample peak area from the standard curve.
3. Multiply the sample concentration by the final extract volume of 10 ml to obtain the total milligrams of extract. Determine the milligrams of analyte per gram of soil sample by dividing the total milligrams of extract by 50 (weight of sampled soil). The value, which is reported in parts per million (ppm), can be obtain by multiplying the milligrams of extract per gram of soil by 20.

4. Analyze calibration standards during the same time as the soil sample analyses; conduct all analyses in duplicate. Generate a standard curve with a minimum of three concentrations ranging from 5 to 100 µg/ml. Spike soil samples with known quantities of CS or CEA and obtain percent recovery to determine the extraction efficiency.

Equipment and Chemical List

1. Equipment:
   a. High Performance Liquid Chromatograph Model 6000A (Waters Assoc.) with the following conditions:
      - variable wavelength UV detector
      - µ-Bondapak CN column
      - mobile phase - 20% (v:v) methylene chloride in hexane
      - flow rate of 1.0 ml/min
      - system pressure - 100 to 450 psi
      - UV detection at 260 nm, 0.01 absorbance units full scale
      - injection volume - 50 µl into a 2 ml injection loop
   b. Soxhlet extraction apparatus
   c. Kuderna-Danish apparatus
   d. Steam bath plate
   e. 250 ml separatory funnel with Teflon stopcock
   f. Glass flasks in various volumes
   g. Glass wool
   h. 100-µl syringe, Whatman cellulose 35 x 94 mm.
2. Reagents:
   a. Anhydrous sodium sulfate, ACS grade
   b. Methylene chloride, HPLC grade
   c. Hexane, HPLC grade
   d. Methanol, HPLC grade
   e. Standards:
      - standard stock - 100 mg of CS or CEA dissolved in 1 ml of methylene chloride
      - calibration stock - 250 µl of standard stock with 50 ml 20% (v:v) methylene chloride in hexane
      - working standards - at least three solutions ranging in concentration of 5 to 100 µg/ml of CS or CEA. Can be prepared by diluting µl quantities of calibration stock in 20% methylene chloride in hexane
      - spiking standards - for CS 125 mg/ 1 ml of methylene chloride and for CEA 100 mg/ 1 ml of methylene chloride. Soil samples are spiked with µl quantities of spiking standards.

Air Samples — Kaipainen, Kostiainen, and Riekkola (1992)

Sample Collection, Transport, and Storage QA/QC

Using Tenax TA absorptive tubes, collect 20 dm^3 of air from approximately 5 to 10 cm above the ground. The temperature at the time of collection should range from -5 to 5°C.

Sample Preparation

1. Place the absorption tubes in a desorption oven and heat to 250°C for 5 minutes.
2. Purge the desorbed compound with helium (10 ml/min) into a cold trap containing a silica capillary column (SE-54, 25-cm in length). Maintain the cold trap at -90°C with liquid nitrogen.
3. Then immediately heat the cold trap to 250°C for 5 minutes and thermally inject the compounds into columns leading to various detectors.

Separation and Detection Parameters

1. Identify the analyte by the retention index monitoring system, which uses response ratios for the different detectors to determine the correct retention time of the analyte. Use M series standards with TID and C series standards with FID and PID. Analyze the pure standards and the standards spiked with urban samples for repeatability and reliability of the retention indices. (See equipment list for the GC set up.)
2. Read the results and collect in duplicates. Use aniline as a reference compound for normalization since all three detectors give a response to aniline.

Equipment and Chemical List

1. Equipment:
   a. Gas chromatograph simultaneously equipped with the following:
      - capillary columns
        - OV-1701 silica capillary column (25 m x 0.32 mm ID, 0.25 µm) is connected to a TID
        - SE-54 capillary column (25 m x 0.32 mm ID, 0.25 µm) is connected jointly through an effluent splitter to an FID and a PID
      - detectors with the following settings:

	TID	FID	PID
Temperature	250°C	250°C	280°C
Lamp energy			10.2 eV
Hydrogen flow	3 ml/min	15 ml/min	
Air flow	80 ml/min	250 ml/min	
Carrier (He) flow	1.5 ml/min	1.5 ml/min	1.5 ml/min
Make-up (He) flow			15 ml/min

- thermal desorption and cold trap unit, connected to the two columns with a ferrule-nut effluent splitter, with the following settings:

Initial temperature of desorption oven	250°C for 5 min
Cold trap temperature	-90°C (maintained with liquid nitrogen)
Carrier gas flow	10 ml/min

- chromatographic data storer (a personal computer having the capability to run MICMAN program).

b. Tenax TA glass packed tubes (17 cm long, 4 mm ID, 6 mm OD)

c. Personal sampling pump.

2. Reagents:

a. Diethyl ether

b. Standard chemical warfare agents including CS

c. C standards (even carbon number C_8-C_{20} *n*-alkanes) for FID and PID

d. M series standards for TID

e. Aniline (1-aminobenzene) used as a reference compound for all three detectors.

13 Dibenz(b,f)-1,4-oxazepine

Use and Properties

Dibenz(b,f)-1,4-oxazepine, also known as CR, is a peripheral sensory irritant, which induces irritation to the eyes, nose, mouth, skin, and the respiratory tract. CR, like CS, is used by civilian law enforcement agencies to control or manage rowdy crowds and by the military for training and terrain denial. CR is high in potency but low in toxicity and is found to be very stable in the environment (Johnson, Haley, and Landis 1990; Keller, Elves, and Bonnin 1986). The formulation of CR used by the military is a mixture of 1% CR with propylene glycol and water (80:20) (Biskup et al. 1975). Table 13-1 lists some common properties of CR.

Table 13-1. Chemical and physical properties of dibenz(b,f)-1,4-oxazepine.

Chemical Name	Dibenz[b,f][1,4]oxazepine
Synonyms	1,4 dibenzoxazepine CR
CAS Registry Number	257-07-8
Molecular Formula	$C_{13}H_9NO$
Molecular Weight	195.22
Physical Description	
Density	
Melting Point	

Possible Methods

Standard Methods

No standard analytical methods for CR have been identified.

Nonstandard Methods

"Toxicity of 1% CR in propylene glycol/water (80/20)" (Biskup et al. 1975):

This report is primarily a toxicology report on the acute and chronic effects of 1% CR on animals. The authors provide a brief method for CR identification using a spectrophotometer with UV detection. However, this report does not contain any information on sample collection and preparation since the CR used in this study is commercially purchased.

"Biodegradation and reduction in aquatic toxicity of the persistent riot control material 1,4-dibenz-oxazepine" (Haley et al. 1990):

This paper primarily describes possible uses of certain strains of bacteria to degrade CR in the aquatic environment. A brief description of an HPLC method in identifying CR and its metabolites in bacterial medium is given. However, the analytical method involving the identification of CR and its metabolite is not very descriptive.

"Analysis of chemical warfare agents in soil samples by off-line supercritical fluid extraction and capillary gas chromatography" (Kuitunen, Hartonen, and Riekkola 1991):

This paper describes a method for identifying chemical warfare agents, including CR, in soil samples. Clean soil samples are spiked with chemical warfare agents to simulate field situations. The analytical method consists of supercritical fluid extraction (SFE) with CO_2 followed by GC analysis with FID and NPD. The analytes are identified by using the retention index monitoring (RIM) system. (This software is provided by the MICMAN program.) The majority of nonpolar or slightly polar compounds were more efficiently recovered (≈89%) with SFE compared to polar compounds. The recovery of CR was more efficient with dichloromethane than with SFE with CO_2.

Development Trends

Abiotic Media

Recent analytical methods for CR include methods using HPLC, HRGC-RIM, and capillary GC with supercritical fluid extraction (Johnson, Haley, and Landis 1990; Kokko 1993; Kuitunen, Hartonon, and Riekkola 1991). Two of these methods sample abiotic mediums such as water and air while the method by Kokko (1993) strictly describes the detection procedures for chemical warfare agents including CR. The extraction process in most cases involves extraction with

dichloromethane or another organic solvent. These methods, with the exception of Kuitunen, Hartonen, and Riekkola (1991), are not listed in the previous section on "Possible Methods" due to lack to detailed technical procedures.

Biotic Media

Analytical methods for detecting CR in biotic matrices were not identified. Some aquatic toxicological studies involving CR were identified; these studies provided very brief descriptions of CR analysis from aqueous samples but the thoroughly described procedures were for toxicological tests (Johnson, Haley, and Landis 1990; Haley et al. 1990; Landis, Chester, and Haley 1993).

Recommended Methods

None of the three methods mentioned above is an ideal field screening method for CR. The first two methods lack description and would be very hard to repeat. The third method is designed to look at the effects of SFE; this extraction process is not suitable for CR extraction. However, due to lack of a better method at the present time, the procedure described by Kuitunen, Hartonon, and Riekkola (1991) is being recommended for field screening of CR in soil. This method relies heavily on the RIM program to identify and quantify compounds being monitored. Table 13-2 lists a brief summary of the recommended nonstandard method for CR analysis.

Table 13-2. Recommended nonstandard method for CR analysis.*

Sample Matrix	Collection and Storage	Preparation Method	Separation Method	Detection Method	Detection Limit	Analysis Cost**
Soil	sieve air dried soil samples through a 2-mm mesh	solvent extract	GC	FID and NPD	not provided	$340

* See Appendix B for a list of the nonstandard methods.

** Estimated total analysis cost, including sample preparation, per sample.

Procedures

Soil Samples — Kuitunen, Hartonen, and Riekkola (1991)

The method by Kuitunen, Hartonen, and Riekkola (1991) detects CR in soil with a capillary GC equipped with an FID and an NPD. The SFE method will not be

described in this section since CR is more efficiently extracted with an organic solvent.

Sample Collection, Transport, and Storage QA/QC

Collect and air dry soil samples. Sieve samples through a 2-mm mesh screen to remove debris before analysis.

Sample Preparation

1. Spike soil samples with 150 µg of CR per gram of soil. Incubate samples at room temperature for 30 minutes before the extraction process.
2. Place 1 gram of soil in a 100-mm x 13-mm diameter culture glass tube and add 1 ml of dichloromethane. Extract the samples in an ultrasonic bath for 10 minutes. Add another 1 ml of dichloromethane and sonicate for another 10 minutes.
3. Filter the supernatant through a 0.5-µm Millex-LCR_{13} filter and collect in 2-ml volumetric flasks. Degas the samples for 3 minutes. The samples are ready for GC analysis.

Separation and Detection Parameters

1. Before analyzing the sample, create the retention index library by determining the retention index of the compounds to be monitored. The retention indices can be stored in the computer and may be used to identify and quantify the analyte in question.
2. Inject a 1-µl sample along with 0.1 µl of retention index standard solution by splitless injection into a capillary column GC connected to an FID and an NPD.
3. Identify and quantify the analyte by the RIM software. Report the concentration in µg of analyte per gram of soil.
4. Analyze the retention index standards and standards used for quantification with the two types of detectors along with samples to ensure proper functioning of the entire GC system.

Equipment and Chemical List

1. Equipment:
   a. Two-channeled GC with the following equipment and conditions:
      - autosampler
      - detectors: FID and NPD
      - personal computer equipped with MICMAN program to provide automatic RIM data
      - injector temperature of 250°C
      - detector temperature of 280°C
      - carrier gas of helium at 2 ml/min
      - capillary column HP-1 and HP-5 with the following dimensions: 25 m x 0.31 mm ID and 0.52 µm film thickness

- pressfit connectors (3 m x 0.32 mm ID)
- deactivated fused silica capillary
- oven temperature programmed at 40°C for 1 min, then ramp up 10°C per min until it reaches 280°C and hold for 10 min

b. Volumetric flasks and culture glass tubes (100-mm x 13-mm)
c. Ultrasonic bath
d. Disposable syringes
e. Millipore Millex-LCR_{13} filters (0.5 µm).

2. Reagents:
   a. Dichloromethane
   b. Ethyl acetate
   c. Standards:
      - TNBP standards for quantification with the NPD
      - Pentadecane (*n*-C_{15}) standard for quantification with the FID
      - retention index standard solutions (M- and C- standard solutions):
        1. M_4-M_{22}, M_3
        2. *n*-C_{10}-*n*-C_{24}
      - chemical warfare agents standard solution.

14 Summary

This report provides a literature review of the methodologies for performing chemical analyses for the components of smokes, obscurants, and riot-control agents. The report examined standard analysis methods for isolating and detecting the components from environmental media (both abiotic and biotic). In cases where standard methods could not be identified, nonstandard analytical methods were reviewed.

The report, which is organized by chapter for each compound investigated, identifies possible analytical methods and recommends the methods that are best suited for measuring the analyte of interest. For each recommended method, summary tables furnish concise information about sample collection, transport, and storage; sample preparation; separation and detection methods; and cost of analysis. In addition, a summary of the recommended standard/nonstandard methods for each compound is provided below. Copies of the recommended methods are furnished in the unattached appendices.

The methodologies discussed in this report are recommended for analyses of field samples for residues of smokes, obscurants, and riot-control agents. Results of such analyses will assist in assessing the potential impacts of smokes, obscurants, and riot-control agents on threatened and endangered species at military installations.

Summary of Recommended Standard/Nonstandard Methods for Components of Smokes, Obscurants, and Riot-Control Agents

Full text for listed methods can be found in unattached Appendices C through O.

Anthraquinone:

-Standard Methods

Matrix	Method References	Total Cost*
Solid Waste	EPA SW-846 Chapter 4, Section 4.1 Sampling Considerations EPA 3500B Organic Extraction and Sample Preparation EPA 3580A Waste Dilution EPA 3611B Alumina Column Cleanup and Separation of Petroleum Wastes EPA 3630C Silica Gel Cleanup EPA 3640A Gel-Permeation Cleanup EPA 8270C Semivolatile Organic Compounds by GC/MS: Capillary Column Technique	$450
Ground Water	EPA SW-846 Chapter 4, Section 4.1 Sampling Considerations EPA 3500B Organic Extraction and Sample Preparation EPA 3510C Separatory Funnel Liquid-Liquid Extraction EPA 3611B Alumina Column Cleanup and Separation of Petroleum Wastes EPA 3630C Silica Gel Cleanup EPA 3640A Gel-Permeation Cleanup EPA 8270C Semivolatile Organic Compounds by GC/MS: Capillary Column Technique	$420
Air	NIOSH Manual Section D, General Considerations for Sampling Airborne Contaminants NIOSH 5506 Polynuclear Aromatic Hydrocarbons by HPLC	$300

-Nonstandard Methods

Matrix	Method Reference	Total Cost*
Plant/ Vegeta-tion	Toth et al. Isolation and determination of alizarin in cell cultures of *Rubia tinctorum* and emodin in *Dermocybe sanguinea* using solid-phase extraction and high-performance liquid chromatography	$350

* Estimated total analysis cost, including sample preparation, per sample.

Brass (Zinc and Copper):

-Standard Methods

Matrix	Method References	Total Cost*
Water	EPA SW-846 Chapter 3, Section 3.1.3 Sample Handling and Preservation EPA 3015 Microwave Assisted Acid Digestion of Aqueous Samples and Extracts EPA 7000A Atomic Absorption Methods EPA 7211 Copper (Atomic Absorption, Furnace Technique) EPA 7951 Zinc (Atomic Absorption, Furnace Technique)	$25
Soil and Waste	EPA SW-846 Chapter 3, Section 3.1.3 Sample Handling and Preservation EPA 3051 Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils EPA 7000A Atomic Absorption Methods EPA 7211 Copper (Atomic Absorption, Furnace Technique) EPA 7951 Zinc (Atomic Absorption, Furnace Technique)	$30
Air	NIOSH Manual Section D, General Considerations for Sampling Airborne Contaminants NIOSH 7300 Elements by ICP	$40
Urine	NIOSH Manual Section F, Special Considerations for Biological Samples NIOSH 8310 Metals in Urine	$130
Blood and Tissue	NIOSH Manual Section F, Special Considerations for Biological Samples NIOSH 8005 Elements in Blood or Tissue	$130

Fog Oil:

-Standard Methods

Matrix	Method References	Total Cost*
Soil	EPA SW-846 Chapter 4, Section 4.1 Sampling Considerations EPA 4030 Soil Screening for Petroleum Hydrocarbons by Immunoassay	$25 per test
Air	NIOSH Manual Section D, General Considerations for Sampling Airborne Contaminants NIOSH 5026 Oil Mist, Mineral	$100
Water and Waste Sludge	APHA 5520C Oil and Grease, Partition-Infrared Method	$50

-Nonstandard Methods

Matrix	Method References	Total Cost*
Soil	Brubaker et al. Environmental Effects of Fog Oil and CS Usage at the Combat Maneuver Training Center, Hohenfels, Germany	$450
Plant	Brubaker et al. Environmental Effects of Fog Oil and CS Usage at the Combat Maneuver Training Center, Hohenfels, Germany	$450

* Estimated total analysis cost, including sample preparation, per sample.

Graphite:

-Standard Methods

Matrix	Method Reference	Total Cost*
Air	NIOSH Manual Section D, General Considerations for Sampling Airborne Contaminants NIOSH 5000 Carbon Black	$100

Hexachloroethane:

-Standard Methods

Matrix	Method References	Total Cost*
Solid	EPA SW-846 Chapter 4, Section 4.1 Sampling Considerations EPA 3500B Organic Extraction and Sample Preparation EPA 3540C Soxhlet Extraction EPA 3550B Ultrasonic Extraction EPA 3620B Florisil Cleanup EPA 3640A Gel-Permeation Cleanup EPA 8000B Determinative Chromatographic Separations EPA 8121 Chlorinated Hydrocarbons by GC: Capillary Column Technique	$150-200
Aqueous	EPA SW-846 Chapter 4, Section 4.1 Sampling Considerations EPA 3500B Organic Extraction and Sample Preparation EPA 3510C Separatory Funnel Liquid-Liquid Extraction EPA 3520C Continuous Liquid-Liquid Extraction EPA 3620B Florisil Cleanup EPA 3640A Gel-Permeation Cleanup EPA 8000B Determinative Chromatographic Separations EPA 8121 Chlorinated Hydrocarbons by GC: Capillary Column Technique	$150-200
Air	NIOSH Manual Section D, General Considerations for Sampling Airborne Contaminants NIOSH 1003 Hydrocarbons, Halogenated	$100

-Nonstandard Methods

Matrix	Method References	Total Cost*
Blood and Tissue	Pellizzari et al. GC/MS Determination of Volatile Halocarbons in Blood and Tissue Pellizzari et al. GC/MS Determination of Volatile Hydrocarbons in Breath Samples	$400

* Estimated total analysis cost, including sample preparation, per sample.

Terephthalic Acid:

-Standard Methods

Matrix	Method References	Total Cost*
Aqueous	EPA SW-846 Chapter 4, Section 4.1 Sampling Considerations EPA 3535 Solid-Phase Extraction (SPE) EPA 3610B Alumina Cleanup EPA 3620B Florisil Cleanup EPA 8000B Determinative Chromatographic Separations EPA 8061A Phthalate Esters by Capillary Gas Chromatography with Electron Capture Detection (GC/ECD)	$320
Solid	EPA SW-846 Chapter 4, Section 4.1 Sampling Considerations EPA 3540C Soxhlet Extraction EPA 3610B Alumina Cleanup EPA 3620B Florisil Cleanup EPA 8000B Determinative Chromatographic Separations EPA 8061A Phthalate Esters by Capillary Gas Chromatography with Electron Capture Detection (GC/ECD)	$350

-Nonstandard Methods

Matrix	Method Reference	Total Cost*
Urine	Hoshi & Kuretani. Metabolism of Terephthalic Acid, Absorption of Terephthalic Acid from Gastrointestinal Tract and Detection of Its Metabolites	$300

Titanium Dioxide:

-Standard Methods

Matrix	Method References	Total Cost*
Water and Waste Water	EPA 200.7 Determination of Metals and Trace Elements in Water and Wastes by ICP-AES	$50
Solid Waste	EPA 200.7 Determination of Metals and Trace Elements in Water and Wastes by ICP-AES	$50
Air	NIOSH Manual Section D, General Considerations for Sampling Airborne Contaminants NIOSH 7300 Elements by ICP	$40
Urine	NIOSH Manual Section F, Special Considerations for Biological Samples NIOSH 8310 Metals in Urine	$130

* Estimated total analysis cost, including sample preparation, per sample.

Red and White Phosphorus:

-Standard Methods

Matrix	Method References	Total Cost*
Water	EPA 7580 White Phosphorus (P_4) by Solvent Extraction and Gas Chromatography	$130
Soil and Sediment	EPA 7580 White Phosphorus (P_4) by Solvent Extraction and Gas Chromatography	$130
Air	NIOSH Manual Section D, General Considerations for Sampling Airborne Contaminants NIOSH 7905 Phosphorus	$100

Polyethylene Glycol:

-Standard Methods

Matrix	Method Reference	Total Cost*
Waste Water	EPA 1673 Poly(ethylene glycol)-600 by Derivatization and High-Pressure Liquid Chromatography	$400

-Nonstandard Methods

Matrix	Method Reference	Total Cost*
Urine	Schwertner et al. New extraction procedure and high-performance liquid chromatographic method for analyzing polyethylene glycol-400 in urine	$300

(o-Chlorobenzal)malononitrile:

-Nonstandard Methods

Matrix	Method References	Total Cost*
Soil	Brubaker et al. Environmental Effects of Fog Oil and CS Usage at the Combat Maneuver Training Center, Hohenfels, Germany Jones & Grady. Analytical methods development and analysis of Camp Simms soil samples for o-Chlorobenzylidenemalononitrile and o-Chlorobenzaldehyde	$450
Air	Kaipainen et al. Identification of Chemical Warfare Agents in Air Samples Using Capillary Column Gas Chromatography with Three Simultaneous Detectors	$340

Dibenz(b,f)-1,4-oxazepine:

-Nonstandard Methods

Matrix	Method Reference	Total Cost*
Soil	Kuitunen et al. Analysis of Chemical Warfare Agents in Soil Samples by Off-Line Supercritical Fluid Extraction and Capillary Gas Chromatography	$340

* Estimated total analysis cost, including sample preparation, per sample.

Acronyms and Abbreviations

AAS	atomic absorption spectrophotometry
ACGIH	American Conference of Governmental Industrial Hygienists
AES	atomic emission spectroscopy
AOAC	Association of Official Analytical Chemistry
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
CAA	Clean Air Act
CAS	Chemical Abstracts Service
CCC	calibration check compounds
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CERL	Construction Engineering Research Laboratory
CR	Dibenz(b,f)-1,4-oxazepine
CS	(o-Chlorobenzal)malononitrile
DCP-AES	direct current plasma argon emission spectroscopy
DFTPP	decafluorotriphenylphosphine
DMSO	dimethyl sulfoxide
ECD	electron capture detector
EDXA	energy dispersive x-ray analysis
EI	electron impact
EICP	extracted ion current profile
EPA	Environmental Protection Agency
FID	flame ionization detector
FLAAS	flame atomic absorption spectrophotometry

FPD	flame photometric detector
GC	gas chromatography
GC/ECD	gas chromatography with electron capture detection
GC/FT-IR	gas chromatography/Fourier transform infrared spectrometry
GC/MS	gas chromatography/mass spectroscopy
GFAAS	graphite furnace atomic absorption spectrophotometry
HC	hexachloroethane
HPLC	high performance liquid chromatography
HPLC/GC	high performance liquid chromatography/gas chromatography
HRGC-RIM	high resolution gas chromatography-retention index monitoring
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
ID	inner diameter
IPC	instrument performance check
IR	infrared
K-D	Kuderna-Danish
LC	liquid chromatography
MCE	mixed cellulose ester
NICI	negative ion chemical ionization
NIOSH	National Institute for Occupational Safety and Health
NPD	nitrogen phosphorus detector
NTU	nephelometric turbidity unit
OSHA	Occupational Safety and Health Administration
P_4	white phosphorus
PAH	polycyclic aromatic hydrocarbon or polynuclear aromatic hydrocarbon
PEG	polyethylene glycol
PICI	positive ion chemical ionization
PID	photoionization detector
PTFE	polytetrafluoroethylene

RCRA	Resource Conservation and Recovery Act
RIM	retention index monitoring (software)
SEM	scanning electron microscope
SERDP	Strategic Environmental Research and Development Program
SFE	supercritical fluid extraction
SIC	spectral interference check
SPCC	system performance check compounds
SPE	solid-phase extraction
STEM	scanning transmission electron microscope
TC/MS	thermal chromatography/mass spectrometry
T&E	threatened and endangered (species)
TID	thermionic detector
TLC	thin layer chromatography
TLV	threshold limit value
TPH	total petroleum hydrocarbon
UV	ultraviolet
WEF	Water Environment Federation
WP	white phosphorus

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